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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

RUBBER. Issued by the United States Tariff Commission, Washington 25, D. C. 6 x 9 in. 102 pp.—This report is one of a series that the Tariff Commission is preparing in response to requests from the Senate Committee on Finance and the House Committee on Ways and Means. These reports cover the principal domestic industries which have been affected favorably or unfavorably by war changes. The current report describes the prewar rubber situation, including the influence of restriction of exports by the governments of the principal rubber-producing countries, and discusses the postwar probabilities and possibilities as to the consumption of rubber in the United States and the world as a whole. The capacity for producing both natural and synthetic rubber and the conditions of competition between both products are also discussed. The various considerations that should be taken into account in determining the postwar rubber policy of the United States are pointed out. One conclusion is that no long-range international agreement on rubber should be made now, since it will take the combined resources of both crude and synthetic rubber producers to meet world demand for rubber for a year or two after the end of the war, although studies leading to such an agreement should be launched as soon as possible. [From *The Rubber Age* of New York.]

HIGH POLYMERS. Published by the New York Academy of Sciences, Central Park West at 79th St., New York City. 6¼ x 9¼ in. 180 pp. \$2.00.—This booklet, taken from the Annals of the New York Academy of Sciences (Vol. XLIV), consists of a series of papers delivered at a conference on high polymers held by the Section of Physics and Chemistry of the Academy on January 8 and 9, 1943. Eight papers were presented, all of which are included in the booklet, together with an introduction by R. M. Fuoss, their titles and authors being as follows:

Recent Results on the Kinetics and Elementary Steps of Polyreactions, J. Abere, G. Goldfinger, H. Mark and H. Naidus; *Elasticity and Flow in High Polymers*, Robert Simha; *Rigidities of Solutions of Polymers*, John D. Ferry;

Intermolecular Forces and Chain Configuration in Linear Polymers: The Effect of N-Methylation on the X-Ray Structures and Properties of Linear Polyamides, W. O. Baker and C. S. Fuller; *Some Aspects on the Mechanism of Addition Polymerization*, Charles C. Price; *Rate Theory and Some Physical and Chemical Properties of High Polymers*, H. M. Hulburt, R. A. Harman, A. V. Tobolsky and Henry Eyring; *Statistical Theory of Chain Configuration and Physical Properties of High Polymers*, Paul J. Flory and John Rehner, Jr.; *Thermodynamic Properties of Solutions of High Polymers: The Empirical Constant in the Activity Equation*, Maurice L. Huggins.

It will be realized from the titles of the papers above that the program was organized to combine different points of view. For example, reaction mechanism is discussed from both the experimental and theoretical aspects, while evidence concerning structure as obtained by the methods of organic chemistry and by x-ray technique is presented. Publication of these papers should prove a valuable contribution to the literature on high polymers. [From *The Rubber Age* of New York.]

SYNTHETIC RUBBER DATA. Western Felt Works, 4115 Ogden Ave., Chicago, Ill. 70 pages.—The data in this manual were largely developed from research on aeronautical problems. The first section is concerned with product data on moulded and extruded synthetic rubber shapes; sheets, rolls, and cut synthetic rubber parts; and various types of seals. A second section evaluates properties of several synthetic rubber compounds and blends. More space is devoted to a comparison of various special synthetic compounds with Army Air Corps specifications, United States Navy specifications, and the aeronautical materials specifications of the Society of Automotive Engineers after exposure to oil, fuel, and solvents. [From the *India Rubber World*.]

THE PREPARATION OF PLANTATION RUBBER IN CEYLON. Revised Edition, 1943. Issued by the Rubber Research Scheme (Ceylon), T. E. H. O'Brien, Director, Research Laboratories, Dartonfield, Agalawatta, Ceylon. Board covers, 9 by 5½ inches, 50 pages. Index.—This volume was prepared to replace a previous edition published in 1929. It describes the methods of preparation of smoked sheets, pale crepe, and lower crepe grades now recommended in Ceylon, without special reference to limitations imposed by wartime shortages of materials and equipment. Each step of preparation and processing is carefully detailed, and defects and their causes in the finished products with suggested remedies are given. Proper methods of tapping and latex collection in the field, treatment of latex in the factory, and the packing of rubber for transportation are also briefly discussed.

Plans for a modern smoked-sheet factory with a tunnel-type smoke house, and a crepe factory with a warm-air drying house, each of 2,000 pounds per day capacity, are reproduced. Throughout the book the necessity of cleanliness and exactness in all operations is stressed, as well as the proper maintenance of machinery and equipment. This concise guide to standard methods should prove valuable to Ceylon producers as a means of achieving uniformity of quality of plantation rubber, which in the past has shown important variations in such properties as rate of vulcanization, plasticity, and aging after vulcanization. [From the *India Rubber World*.]

COLLOID CHEMISTRY, THEORETICAL AND APPLIED. By Selected International Contributors. Collected and Edited by Jerome Alexander. Vol-

ume V. Theory and Methods. Biology and Medicine. Reinhold Publishing Corporation, 330 West 42nd Street, New York, N. Y., 1944. vi × 1256 pp. Illustrated. 16 × 24 cm. Price, \$20.00. This present volume is the fifth in this widely and favorably known series. The Editor, because of wartime conditions, was not able to secure as worldwide a representation of authors as in the previous volumes, but he has nevertheless assembled contributions from a distinguished group of chemists, physicists, biologists and physicians in this country. The sixty essays in this book, varying in length from five to ninety pages, cover a vast field of the natural sciences. They are arranged in two nearly equal sections, the first dealing with the theory and methods of colloid chemistry, the second with its applications to biology and medicine. Each essay recounts the present status of, and the latest developments in, its special field, presenting the subject matter particularly from the point of view of the author's own researches. To be sure, the classification of some of them under colloid chemistry may be far-fetched, but one is glad that they have been included. The great variety and excellence of the essays is a tribute to the versatility of the Editor, to his enthusiastic interest in the fundamental phenomena of chemistry and biology, and to his evangelistic devotion to colloid chemistry. I have but one regret to register. It is too bad to publish or rather to embalm these excellent and stimulating essays in such an awkward, bulky and expensive tome. They should have been issued in several instalments, separately purchasable and of a size that could be conveniently transported, held and read by an ordinarily robust human being. [Abridged from the *Journal of the American Chemical Society*.]

THE PROCESS OF EXTRUDING. Industrial Products Division, B. F. Goodrich Co., Akron, Ohio. 8½ x 11 in. 80 pp.—Comprehensive data for industrial engineers and designers about the process of extruding and products that can be made thereby from natural, synthetic and reclaimed rubber and from plastics is contained in this illustrated combined catalog and manual. The process of extruding is described, as is the manufacturing equipment, die-making, compounding, milling match testing, special constructions and conventional and complicated shapes. A discussion of manufacturing limitations is also included. [From *The Rubber Age* of New York.]

VOLUME CORRECTION FACTORS FOR C₄ HYDROCARBON MIXTURES. Compiled by C. S. Cragoe. Letter Circular LC-757. National Bureau of Standards, United States Department of Commerce, Washington, D. C. 23 pages.—Compiled at the request of the Rubber Reserve Co. to facilitate accurate determinations of quantities in containers at existing temperature and pressure and to supplement previous compilations, the tables in this pamphlet apply to mixtures consisting entirely of C₄ hydrocarbons and C₄ mixtures containing limited amounts of C₃ and C₅ hydrocarbons which come within the range of 40 to 80 lbs. per sq. in., absolute, vapor pressure at 100° F, and the range 0.56 to 0.63 specific gravity at 60°/60° F. The tables should prove useful in commercial transactions and in checking inventories. [From the *India Rubber World*.]

COMMERCIAL METHODS OF ANALYSIS. By Foster Dee Snell and Frank M. Biffen. Published by McGraw-Hill Book Co., 330 West 42nd St., New York, N. Y. 5½ x 8¼ in. 754 pp. \$6.00.—Although many meritorious books have been published on theoretical analytical chemistry, this book

differs from all in that it shows the method of approach to the analysis of innumerable complex commercial products, including rubber and the synthetic elastomers, on the market today. Many of these materials are colloids, some are emulsions containing ingredients other than or in addition to water and oil, a majority contain organic as well as inorganic ingredients. Procedures and calculations for hundreds of determinations are given in the book, as well as many pointers on the general approach to analysis of unknown samples and on the reasons behind many steps of the work. Special emphasis is laid on time-saving methods, sufficiently exact for the required purpose in the efficient laboratory. Many modern methods of analysis and methods for analyzing of substances of recent importance, such as synthetic plastics and synthetic elastomers, have been included, even when only qualitative information is available. The useful new branch of qualitative analysis by spot tests is condensed into a single chapter. Analytical methods applied to rubber are covered in two separate chapters, one devoted to "Rubber" and the other to "Miscellaneous Rubber Analyses and Synthetic Elastomers," the latter actually a continuation of the former. The entire gamut of rubber analysis is covered, from both qualitative and quantitative standpoints. To make the book of more universal use, standard methods, such as those devised by the American Society for Testing Materials and the Association of Official Agricultural Chemists, are outlined, though often not in the exact words of the methods themselves. The book has 39 chapters in all, and an excellent cross-referenced index. Although designed for constant use by the experienced analyst who wishes aid in selecting best methods for various products and quick reference to complete, rapid methods of many types, it should also prove valuable to the newer chemist in developing a sure technique in commercial analytical work. [From *The Rubber Age* of New York.]

INFLUENCE OF HUMIDITY ON THE RESISTIVITY OF SOLID DIELECTRICS AND ON THE DISSIPATION OF STATIC ELECTRICITY. By E. M. Cohn and P. G. Guest. Bureau of Mines, U. S. Department of the Interior, Washington, D. C. 8 x 10½ in. 42 pp.—Most of the important contributions dealing with the electrical conductivity of solid dielectrics, including all its aspects and its relationships to other physical properties of these materials, have been listed and abstracted in this information circular, which includes also some general references on static electricity. Methods and removing static charges are described, methods of and conditions for measurements of resistivity are discussed, equations for the calculation of resistivity are given, and methods of resistance measurements *in situ* are reviewed. Three tables showing the resistivity of various dielectrics at different humidities are included. An appendix contains a short development of the mathematical formulation of the charging and discharging currents due to interfacial polarization. [From *The Rubber Age* of New York.]

STANDARDS ON TEXTILE MATERIALS. Prepared by Committee D-13 on Textile Materials. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia 2, Penna. 6 x 9 in. 490 pp. \$2.75.—This latest edition of the standards on textile materials issued by the A.S.T.M. through the work of Committee D-13 on Textile Materials includes more than 75 standard specifications, texts and definitions developed by the Society. In addition, it contains other pertinent related information, including useful charts and tables, proposed specifications and tests, and abstracts of technical

papers. In the section on standards, comprising the major portion (365 pages) of the book, standards on general subjects are given first, such as definitions, requirements on testing machines, tests to evaluate fire retardant properties, resistance to insect pests, microorganisms, water, etc.; the specifications covering specific textiles follow. These cover asbestos, bast and leaf fibers, cotton (the largest section), glass, rayon and silk, wool and others. Appended material includes a yarn number conversion table and a relative humidity table, a proposed universal yarn numbering system, and a test published for information covering evaluation of the properties relating to the hand of certain fabrics. Abstracts of papers presented at the 1944 Committee D-13 Meeting are included. These cover the Cotton Testing Service; this Service from the Viewpoint of the Breeder; Raw Materials Problems; Grex Universal Yarn Numbering System; and Quality Control in the Supply of Textiles to the Armed Forces. [From *The Rubber Age* of New York.]

1944 SAE HANDBOOK. Society of Automotive Engineers, Inc., 29 W. 39th St., New York 18, N. Y. Cloth, $5\frac{1}{4}$ by $8\frac{1}{2}$ inches, 848 pages. Index. Price \$5.—Wartime industrial and technical progress in developing new methods and materials facilitating production is reflected in the new and revised standards and specifications in the latest annual edition of the official publication of the SAE. Specifications for medium and heavy-duty coolant hoses formulated by the joint ASTM-SAE Technical Committee A on Automotive Rubber are primarily of value as a guide in the selection of materials for use in combat vehicles and others used for less critical and exacting services. Oil-resisting synthetic rubbers are required for combat vehicles; all-reclaim rubber compounds, for moderate-duty coolant hoses. The Classifications and Physical Requirements for Rubber Compounds specifications have been revised as of January 15, 1944. They are intended as an aid in selecting compounds for automotive and aeronautical rubber. Compounds for tires, tubes, sponge rubber, and hard rubber are not included. The physical requirements are considered adequate as substitutes for both war materials and most ordinary normal requirements.

Cancellations include specifications for rubber hose, clamps, and fittings as published in the 1943 edition. [From the *India Rubber World*.]

THE ELECTRON MICROSCOPE. By E. F. Burton and W. H. Kohl. Published by Reinhold Publishing Corp., 330 West 42nd St., New York City. 6 x 9 in. 234 pp. \$3.85.—This book outlines the basic principles of both optical and electron microscopes, with high points in the discussion graphically illustrated by original line-drawings. After a detailed description of the dual nature of light, its application to the functioning of the electron microscope is shown, with frequent emphasis being placed on the contributions of Newton, Maxwell, de Broglie, and Planck. The book is high-lighted by numerous striking photographs of bacteria and industrial substances, such as asbestos, carbon blacks, and oxides. The authors of the book, assisted by James Hillier, developed and built the first compound electron microscope in America. There are 17 chapters in all, plus a general bibliography and a subject index. [From *The Rubber Age* of New York.]

LIST OF AVAILABLE PUBLICATIONS OF THE DEPARTMENT OF COMMERCE. Compiled and indexed by Thelma C. Ager and Franklin L. Thatcher. United States Government Printing Office, Washington, D. C. 1944. 202 pages.—Available publications of the National Bureau of Standards, Bureau of Foreign

and Domestic Commerce, Bureau of the Census, Civil Aeronautics Administration, and other bureaus of the Department of Commerce are included in this indexed list. Many scientific and economic studies of rubber and rubber products are catalogued. [From the *India Rubber World*.]

USES AND APPLICATIONS OF CHEMICALS AND RELATED MATERIALS. Volume II. Compiled and edited by Thomas C. Gregory. Based on data published in the *Oil, Paint, and Drug Reporter*. Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1944. Cloth, 9 by 6 inches, 528 pages. Price \$9.—Volume I of this compilation, published in 1939, listed 5167 substances and their industrial uses. Volume II covers 2642 additional chemicals and related materials and their industrial applications. Also included is an index of uses covering both volumes and arranged by a classification or grouping based on the function for which the material is used. There is an index of synonyms and cross-references, an index of United States and British patents cited in the "Uses and Applications" sections of both volumes, and a list of the names and addresses of the owners of the patents. The makers, the sellers and the users of chemicals, as well as technical workers, research bureaus, and libraries, will find this compilation of chemical facts a useful directory. [From the *India Rubber World*.]

CHEMICAL ENGINEERING NOMOGRAPHS. Dale S. Davis. Published by McGraw-Hill Book Co., Inc., 330 W. 42nd St., New York, N. Y. 1944. Cloth, 9 by 5¼ inches, 320 pages. Index. Price, \$3.50.—The frequent and practical use of nomography in the chemical and process industries during the past few years has shown the value of nomographs as an efficient reference tool for simplifying and expediting the calculations of chemical engineers and analytical, control, and physical chemists. The author of this volume, who is mathematician for the Wyandotte Chemicals Corp., has included many of his own nomographs and the alignment and line-coördinate charts of others, all heretofore available only in the periodical technical literature of the past 15 years. The 200 charts presented are supplemented with directions for their use and with material indicating their application, limitations, and validity. About 100 of the charts present physical property values. There are several vapor-pressure charts, and data on viscosity, density of solutions, specific heat, pH, and gas solubility. Other charts cover the flow of fluids and the contents of horizontal tanks. The charts are readily usable in the standard book-size page. Some require a reference line, but the majority are of the simple three-scale type and may be read with a flat edge. [From the *India Rubber World*.]

CHEMICAL ENGINEERING CATALOG: 1944-45. Published by Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 8 x 11 in. 1580 pp.—This is the 29th edition of the process industries' catalog, and despite wartime paper restrictions and other limitations, it is larger than the previous edition. As usual, the bulk of the book is made up of manufacturers' catalogs, divided into equipment and supplies and chemicals and materials, with classified indexes appearing with each section. In addition, it includes an alphabetical index of firms represented in the catalog, a trade name index revised and brought completely up-to-date, and a technical and scientific books section. Paper restrictions have unfortunately limited the listing of books in the latter section to a selected list of those offered by participating technical publishers. [From *The Rubber Age* of New York.]

THE MOLECULAR WEIGHTS OF RUBBER AND RELATED MATERIALS

V. THE INTERPRETATION OF MOLECULAR WEIGHT MEASUREMENTS ON HIGH POLYMERS*

GEOFFREY GEE

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The relative merits of the osmotic and viscosity methods for the determination of the molecular weights of high polymers have been widely discussed. The purpose of this paper is to present a new theoretical justification for the osmotic method, and to draw attention to the conditions under which the viscosity method may be employed.

OSMOTIC PRESSURE MEASUREMENTS

The experimental details of osmotic pressure measurements on high polymer solutions have been described recently by a number of authors¹. The results give the osmotic pressure π of the solution as a function of the polymer concentration C . The problem to be considered here is that of deducing the molecular weight M of the polymer from these data. The classical osmotic pressure equation is that of van't Hoff:

$$\frac{\pi}{c} = \frac{RT}{M} \quad (1)$$

according to which π/c should be independent of C and equal to $\frac{RT}{M}$. In general, polymer solutions do not obey this law, but π/C increases approximately linearly with C , the slope depending on the nature of the solvent. An illustration of this behavior is given by Fig. 1 showing some of Dobry's measurements of the osmotic pressure of nitrocellulose in various solvents². These results show that the limiting value of π/C at infinite dilution is the same for all the solvents examined. No case has been reported in which this has been proved to be untrue, but in the case of polymers of very high molecular weight, it is not usually possible to demonstrate it with certainty, owing to the difficulty of extrapolating data showing a large slope. This problem of extrapolation furnishes one of the major experimental difficulties of the osmotic method, and is perhaps best dealt with by choice of a solvent which reduces the dependence³ of π/C on C . Having estimated the limiting value (π/C_0), we write:

$$\left(\frac{\pi}{C} \right)_0 = \frac{RT}{M} \quad (2)$$

Before one can place any reliance on molecular weights derived from Equa-

* Reprinted from the *Transactions of the Faraday Society*, Vol. 40, No. 6, pages 261-266, June 1944.

tion (2), it is necessary to consider its theoretical basis. By thermodynamic reasoning, it may be shown that, for dilute solutions of any solute⁴:

$$\Pi V_0 = -\Delta G_0 = T\Delta S_0 - \Delta H_0 \quad (3)$$

where V_0 is the molar volume of the solute and ΔG_0 , ΔS_0 , ΔH_0 are the increases in Gibbs' free energy, entropy and heat content when one mole of solvent is added to a large bulk of solution. For ideal solutions, $\Delta H_0 = 0$, and Equation (3) gives a relation between the osmotic pressure and the entropy of dilution ΔS_0 . Now it is possible to calculate ΔS_0 statistically for simple systems by making use of Boltzmann's equation⁵ relating the entropy S of a system with its probability P :

$$S = k \ln P. \quad (4)$$

Thus, if the solute and solvent molecules are of similar size, we may calculate P , and therefore S , by considering the number of ways of arranging the mole-

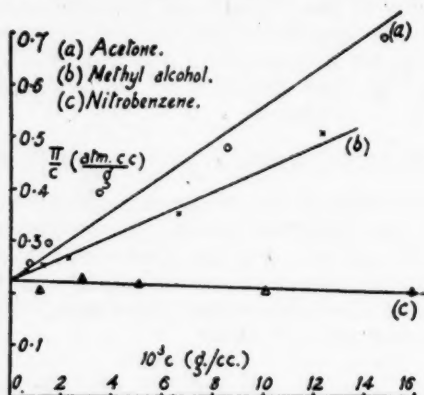


Fig. 1.—Osmotic pressures of nitrocellulose solutions at 22° C.

cules on a pseudocrystal lattice. It is readily shown in this way that the entropy of dilution is given by⁶:

$$\Delta S_0 = R \ln \left(1 + \frac{N_s}{N_0} \right) \quad (5)$$

where N_s , N_0 are the numbers of solute and solvent molecules in the mixture. For dilute solutions, the log term may be expanded, giving:

$$\Delta S_0 \simeq RN_s/N_0 \simeq \frac{RV_0}{M} C. \quad (6)$$

If $\Delta H_0 = 0$, substitution of (6) into (3) leads at once to van't Hoff's law. If ΔH_0 is not negligible, it may be shown statistically⁷ that, for dilute solutions,

$$\Delta H_0 = \alpha V_0 C^2 \quad (7)$$

where α is a constant.

Hence

$$\frac{\Pi}{C} = \frac{RT}{M} - \alpha C. \quad (8)$$

from which Equation (2) follows at once.

The problem of calculating ΔS_0 becomes much more difficult when the solute molecules are large, but an approximate solution has been obtained⁸ for the special case that the polymer consists of long flexible chains which may be regarded as divisible into segments, each the size of a solvent molecule, with complete freedom of rotation between segments. It has been shown that this model leads to an equation of the same form as (8), and therefore that Equation (2) is satisfied. This model is clearly too simple to be applicable to polymer solutions generally, but in the next section it will be shown that Equation (2) is in fact applicable to solute molecules of any size and shape.

LIMITING FORM OF THE ENTROPY OF DILUTION

We consider the arrangement, on a lattice of $N_0 + nN_s$ sites, of N_0 solvent molecules, each occupying one site, and N_s polymer molecules, each requiring n sites, and we confine our attention to highly dilute solutions, so that $nN_s \ll N_0$. The lattice is to be filled by arranging the polymer molecules first, and it is evident that all the sites are available to the first segment of the first polymer molecule. Having fixed the first segment, the number of ways of arranging the remaining segments of this molecule will be some definite number, p_1 , say, which depends on the size, shape and flexibility of the polymer molecule. The total number of arrangements of the first polymer molecule on the lattice will thus be $p_1(N_0 + nN_s) \approx p_1N_0$. If the solution is sufficiently dilute, there will be very nearly the same number of ways of arranging each remaining polymer molecule, since interference of one polymer with another will be negligible. Hence the total number of ways of arranging the N_s polymer molecules will be approximately $(p_1N_0)^{N_s}$. The number of ways of arranging these N_s polymer molecules on nN_s sites, *i.e.*, in the pure polymer, is unknown, but we may write it as p_2 . Using Boltzmann's equation, the increase of entropy $\Delta S_{N_0}^m$ on mixing the N_s polymer molecules with N_0 solvent molecules is seen to be:

$$\Delta S_{N_0}^m \approx k \{ N_s \ln (p_1 N_0) - \ln p_2 \}. \quad (9)$$

Repetition of this calculation with the number of solvent molecules increased by δN_0 gives for the entropy of mixing $\Delta S_{N_0 + \delta N_0}^m$ of N_s polymer molecules with $(N_0 + \delta N_0)$ solvent molecules:

$$\Delta S_{N_0 + \delta N_0}^m \approx k \{ N_s \ln p_1 (N_0 + \delta N_0) - \ln p_2 \}. \quad (10)$$

Now, by definition:

$$\Delta S_0 = N_{\delta N_0 \rightarrow 0} \lim_{\delta N_0 \rightarrow 0} \frac{1}{\delta N_0} (\Delta S_{N_0 + \delta N_0}^m - \Delta S_{N_0}^m) \quad (11)$$

where N is Avogadro's number.

Substituting from (9) and (10) in (11):

$$\Delta S_0 \approx R \frac{N_s}{N_0} \approx R \frac{V_0}{M} C. \quad (6)$$

Since it has already been assumed that the solution is so dilute that polymer-polymer contacts are negligible, it follows that further dilution does not change the number or nature of the intermolecular contacts, so $\Delta H_0 = 0$. A better way of expressing this conclusion is to say that it is evident from this model that, at sufficiently high dilution, ΔH_0 becomes negligible compared with $T\Delta S_0$.

It follows, therefore, that van't Hoff's law is the correct limiting law at infinite dilution, whatever may be the size and shape of the solute molecules.

If we write van't Hoff's equation in the form:

$$\Pi = \frac{kT}{V} \cdot N, \quad (12)$$

where V is the volume of solvent in which N , solute molecules are dissolved, it is evident that what we actually obtain by osmotic measurements is the number of solute molecules, *i.e.*, the number of kinetically distinct units of solute. If each of these is associated with a number of solvent molecules, the latter will not be included in the molecular weight. If, however, two or more solute molecules are associated with each other, the molecular weight found is that of the complex. Association of the solvent will have no effect on the result, which is also independent of the nature of the solvent. It will be shown in a subsequent publication that this is also true of mixed solvents.

The above discussion shows that the theoretical basis of the osmotic method is firmly established, and that if $(\Pi/C)_0$ can be found accurately, the absolute molecular weight of the solute—as dispersed in the solvent which has been employed—may be calculated from it with complete confidence.

THE VISCOSITY METHOD

Much the simplest and most widely used method of obtaining the molecular weight of long-chain polymers depends on the measurement of the viscosity of a dilute solution. The theoretical and experimental basis of this has been widely discussed⁹, and all that can be done in this brief paper is to indicate the author's own views as to the usefulness of viscosity measurements.

Various attempts to calculate the viscosity of polymer solutions have led to equations of the general form:

$$[\eta] = KM^\beta \quad (13)$$

where $[\eta]$, the intrinsic viscosity, is the limiting value at infinite dilution of η_{sp}/c , η_{sp} being the specific viscosity of the solution. K , β are constants, the latter being assigned various values between 0 and 2, according to the shape of the polymer molecule in solution, and the particular model used in the analysis. Staudinger's well-known equation is seen to be a special case of (13), with $\beta = 1$. In the present state of the theory, it does not seem possible to calculate absolute values of either K or β for any particular polymer solution, although the theory gives good ground for believing that an equation of the form (13) should hold for a series of polymers differing only in molecular weight. The most convenient way of treating this is to plot $\log [\eta]$ against $\log M$, and in Figure 2 some recent data on fractionated polymers are presented in this way. It is evident that the equation holds over a wide range of M , giving the following values of β :

Cellulose acetate in acetone ¹⁰	$M = 25,000$ to $125,000$ $\beta = 0.67$
Polyisobutylene in cyclohexane ¹¹	$M = 6,000$ to $1,300,000$ $\beta = 0.64$
Rubber in benzene ¹²	$M = 7,000$ to $350,000$ $\beta = 0.96$

The value of β found for rubber in benzene is, within experimental error, unity, so that Staudinger's law holds, whereas it clearly does not hold for the other solutions. It is, however, to be noted from Figure 2 that squalene

($M = 410$) does not fall on the straight line drawn to represent the data for the rubber fractions, so that Equation (13) evidently breaks down for sufficiently low values of M . Similar behavior has been reported for other homologous series¹³, and the empirical relationship:

$$[\eta] = KM + \alpha \quad (14)$$

found to fit. It seems quite probable that a similar correcting term α may need to be added to the more general Equation (13) to extend its application to low molecular polymers.

The discussion so far has been confined to polymers which are believed to be essentially linear in structure, and approximately homogeneous. For such materials it appears that viscosity measurements can be used to measure

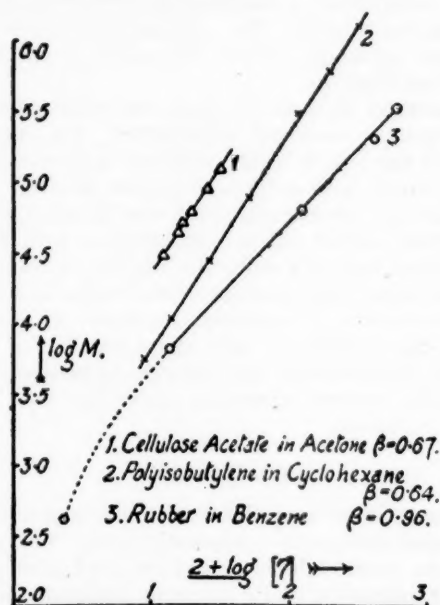


FIG. 2.—Dependence of viscosity on molecular weight.

molecular weights, once values of K and β have been found by calibration against the osmotic method. It is to be noted that K (and possibly to a smaller extent β) depends on the nature of the solvent. We have now to consider what information, if any, can be obtained from viscosity measurements on polymers which are not necessarily either homogeneous or of linear structure.

Confining attention first to linear polymers, it is clear that since the viscosity method applies to homogeneous materials, it must give some sort of average molecular weight for a mixture. This average is not, however, the same as that given by the osmotic method, which is easily seen to conform to the natural definition of an average molecular weight as the total weight of material divided by the total number of molecules. The viscosity average molecular weight of $\sum_i N_i M_i$ molecules of molecular weight M_i ; (where i takes all

values) may be shown to be¹⁴:

$$\bar{M}_{Visc} = \left(\frac{\sum_i N_i M_i^{(1+\beta)}}{\sum_i N_i M_i} \right)^{1/\beta} \quad (15)$$

For $\beta = 1$ this reduces to a weight average¹⁵. For any value of $\beta > 0$ the viscosity average is greater than the osmotic average, and the ratio between them may be approximately 2 for an unfractionated polymer¹⁶. It is evident that if the distribution is unknown, the viscosity alone gives only an approximate molecular weight, though the order of magnitude is correct unless the distribution is very unusual, *e.g.*, a low molecular polymer with a proportion of very high molecular material. When both osmotic and viscosity molecular weights have been determined, a comparison of the two gives a rough idea of the homogeneity of the sample. The method is, however, extremely crude, and the approximate agreement of the two values is not inconsistent with a moderately broad distribution.

The viscosity method becomes of much less value when there is a possibility that the polymer is nonlinear in structure. The intrinsic viscosity depends essentially on the length of the polymer molecules¹⁷ and, for a given molecular weight, should be less for a branched than for a linear structure. This expectation has been abundantly borne out by some work on the thermal degradation of rubber carried out in collaboration with Dr. Bolland¹⁸. Although the osmotic and viscosity molecular weights of many of these products were approximately equal, fractionation showed them to contain a wide range of molecular sizes and to be of branched structure. In some of the fractions the viscosity molecular weight was only about one-half of the osmotic value. In the absence of any fractionation, the osmotic and viscosity molecular weights would have led to the entirely erroneous conclusion that the products were approximately homogeneous.

CONCLUSIONS

Unless an ultracentrifuge is available, absolute molecular weight determinations must be based ultimately on osmotic data. Viscosity measurements furnish a convenient method of interpolation, and give reliable results for homogeneous linear polymers. The viscosity molecular-weight of a typical unfractionated polymer would not be very seriously in error unless the polymer were extensively branched. No reliable conclusions about molecular-weight distribution can be drawn from molecular-weight data alone without carrying out a fractionation, although a useful guide to the homogeneity of a polymer known to be of linear structure is furnished by the ratio of the viscosity and osmotic molecular weights.

ACKNOWLEDGMENT

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THE MAGNETIC ANISOTROPY OF STRETCHED RUBBER AS A FUNCTION OF THE TENSION TO WHICH IT IS SUBJECTED *

EUGÉNIE COTTON-FEYTI

From the standpoint of its magnetic anisotropy, stretched rubber is comparable in a first approximation to a uniaxial crystal, in which the direction of the axis is the same as the direction of elongation. It is possible to measure this anisotropy by means of the oscillation method used by Krishnan, Guha and Banerjee¹ in studying crystals.

The sample to be examined is suspended in a uniform horizontal magnetic field in such a manner that its axis is horizontal. It is then so arranged that the torsion of the suspension wire is zero when the rubber sample is in a position of equilibrium in the field. The times of oscillation T' and T for very small angular displacements around this position, in the presence and then in the absence of the magnetic field, are then recorded. In this way the difference between the specific susceptibilities in the direction of the axis and in the horizontal direction perpendicular to the axis is calculated by application of the equation:

$$\Delta\chi = \frac{c}{mH^2} \cdot \frac{T^2 - (T')^2}{(T')^2} = \frac{c}{mH^2} \cdot \left(\frac{T^2}{(T')^2} - 1 \right)$$

where c is the torsion couple of the suspension wire, H is the field, and m is the mass of the rubber sample.

To measure by this method the anisotropy of a sample of rubber subjected to a known tension, a circular band is wound as uniformly as possible around one diameter of a rigid disc². The disc holding the rubber band is then suspended in a uniform horizontal magnetic field, with its own plane also horizontal. If the disc is isotropic, the measured anisotropy is attributable solely to the rubber, and it is possible to determine the way in which it changes with the number of turns. The weights F which must be suspended on the circular rubber band to stretch it to the elongations corresponding to the different number of turns on the disc are then measured.

As for the equipment and technique³, the discs were of unhardened glass or of Plexiglass free from birefringence. The measurements were made with a field of 23,000 Gauss units. In each series of experiments, the factors c , m and H remained constant, so it was necessary only to compare the values of $[T^2/(T')^2] - 1$. Since T is large in comparison with T' , the $T^2/(T')^2$ values themselves should obviously be proportional to the anisotropy. The tabulated data above summarize some of the results obtained. These measurements show that the anisotropy first increases with increase in the number of turns but then approaches a limiting value. It is probable that the anisotropy increases in proportion to the progressive orientation of the molecular chains

* Translated for RUBBER CHEMISTRY & TECHNOLOGY from *Comptes rendus hebdomadaires des séances de l'académie des sciences*, Vol. 215, No. 15, 299-301, October 12, 1942.

Rubber sample	No. of turns	Length (cm.)	F (grams)	T (S)	T' (S)	$T^2/(T')^2$
No. 1 on a glass disc	2	9.92	56	85	6.2	188
	3	13.88	120	...	5.6	230
	4	19.84	215	...	5.0	289
	5	23.80	280	...	4.9	301
	6	29.76	380	...	4.8	313
No. 1 on a Plexiglass disc	1	9.0	40	400	18.7	45.7
	2	18.0	200	...	17.0	55.3
	3	27.0	305	...	15.3	68.6
	4	36.0	470	...	15.2	69.2
No. 2 on a Plexiglass disc	3	27.0	360	400	10.9	135
	4	36.0	600	...	9.4	182
	5	45.0	820	...	8.7	210
	6	54.0	960	...	8.7	210
Rubber sample No. 1	m = 0.100 g.		= 8.3 cm.			
Rubber sample No. 2	m = 0.950 g.		= 18.8 cm.			
Glass disc	M = 2.05 g.		d = 2.3 cm.	e = 0.18 cm.		
Plexiglass disc	M = 7.47 g.		d = 4.0 cm.	e = 0.5 cm.		

in parallel formation by the effect of the stretching. When the anisotropy reaches its maximum value, all the chains have unquestionably aligned themselves in parallel. Increased tension can of course be brought about by further stretching, but in this case there is no further change in the direction of the molecular chains, and so the anisotropy does not show any further change.

It is of interest to note that the curve of the changes in magnetic anisotropy with change in tension is of the same character, *i.e.*, shows the same trend, as the curve of the changes in intensity of the diffraction spots of x-ray diagrams with change in tension. It is intended next to measure the magnetic anisotropy of samples of rubber, the x-ray diagrams of which are already known, so as to compare the two methods of investigation.

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- ³ The glass and Plexiglass discs were placed at the author's disposal by M. Boutry. All the samples of rubber were kindly furnished by the French Rubber Institute.

FURTHER STUDIES OF THE INFRARED ABSORPTION OF RUBBER *

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INTRODUCTION

The infrared absorption of highly purified natural rubber has been studied by Stair and Coblenz¹, who found that the spectra of the alpha and beta components are almost identical and that aging (oxidation) of rubber is accompanied by increased absorption near 3μ and 6μ and in the region between 7μ and 11μ . Other infrared studies of rubber and related compounds have been made by Williams², Sears³, Wells⁴, and Barnes⁵. The transmission curves obtained in these latter studies are in essential agreement with those of Stair and Coblenz. Minor variations are to be expected in view of the wide variations of the physical properties exhibited by rubber obtained from different sources and processed in different ways.

Williams and Taschek⁶ have studied the effects of elastic stretch on the absorption of rubber between 2μ and 8μ . The shapes of the absorption bands in this region were modified when the material was stretched, but the positions of the absorption maxima remained unchanged. Samples stretched radially to twelve times their original area exhibited minor transmission minima between 4μ and 5μ ; however, these minima were possibly produced by interference effects in the thin absorbing layers. Absorption and reflection coefficients for rubber under various conditions of stretch were calculated from transmission data on samples of different thicknesses at similar elongations. Although there were inherent weaknesses in this method (for example, the assumption that the surface conditions of the samples were the same), the results indicated that stretching produced an increase in the absorption coefficient and a decrease in the reflection coefficient. The absorption coefficients as computed were a measure of the combined effects of true absorption and scattering within the sample; the reflection coefficients were a measure of all surface effects producing decreases in transmission.

The purpose of the present study has been to extend the range of the earlier measurements to 15μ in the hope of detecting any changes in the lower vibrational frequencies produced by stretch and to obtain more accurate data at various wave-lengths on the changes in absorption and reflection coefficients accompanying stretch. In the case of a material like rubber in which there is considerable variation even in samples cut from a single sheet, it is possible to obtain only semi-quantitative data, but it is felt that even data of this type may be useful in the development of adequate theories of the structure of rubber.

EXPERIMENTAL WORK AND RESULTS

The rubber samples used were cut from sheets of vulcanized rubber of low sulfur content⁷. The range of thickness of the unstretched samples was 0.03–

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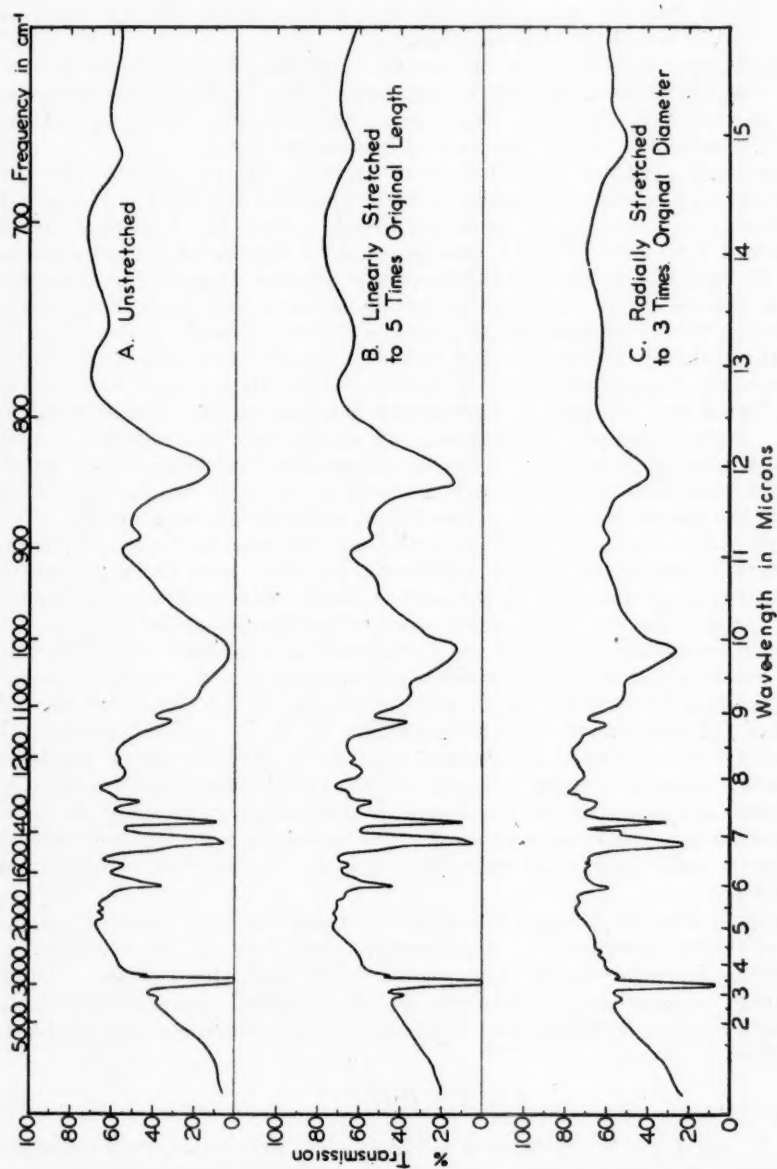


FIG. 1.—The transmission spectrum of rubber: curve A, unstretched rubber; curve B, rubber stretched unilaterally to five times its original length; and curve C, rubber stretched radially to three times its original diameter.

0.07 mm. The thicknesses were measured by means of a micrometer screw equipped with a ratchet. Comparison revealed that the thicknesses of the unstretched material as measured with the micrometer were consistently 12 per cent less than the gauge equipped with a 3-oz. counterweight, which is widely used in industrial work on rubber.

The samples were mounted on metallic supporting frames placed in such a way that the radiation passed through parts of the sample remote from the points of support. The spectrometer was a rocksalt prism instrument of the Littrow type, and has been described by Nielsen and Smith⁸.

The results obtained are indicated in Figure 1. Curve *A* represents the percentage transmission of a single layer of unstretched rubber. This curve is similar to the transmission curves published by Stair and Coblenz¹ except for a strong band near 9.5μ and weak bands at 6μ and 3μ produced by oxidation. It should be noted that the transmission is low at short wave-lengths, even in regions where there are no strong characteristic absorption bands. Curve *B* shows the transmission of a sample stretched linearly to five times its original length. It will be observed that the positions of the major absorption bands remain unchanged except in the case of the strong band near 11.9μ , which has shifted to shorter wave-lengths and has become asymmetrical in shape. Curve *C* gives the transmission of a sample stretched radially to three times its original diameter. To obtain measurable absorption in the minor bands, it was necessary to place two sheets in the light beam. Hence, in curve *C* the decreases in transmission due to reflection are exaggerated. The positions of the absorption bands in curve *C* are the same as in curve *A* within the limits of experimental error. Although the band near 11.9μ is slightly asymmetrical, the magnitude of the shift to shorter wave-lengths is not appreciably greater than the experimental error in locating absorption maxima.

To determine the position of the 11.9μ band as a function of stretch, this region was carefully studied for samples stretched linearly by various amounts up to 6 times the original length and radially up to 3.5 times the original diameter. Typical results are shown in Figure 2. In the case of linear stretch the position of the band is not changed appreciably until the sample has been stretched to 4 times its original length, but changes position rapidly as greater elongations are attained. As linear stretch of the sample increases, the band becomes more and more asymmetrical. The curves for radial stretch indicate changes in band shape, but very little shift in the position of maximum absorption.

To determine the changes in absorption coefficient with changing conditions of stretch, transmission measurements were made at the positions of maximum absorption in the 3.3μ , 6.9μ , 7.3μ , and 11.9μ bands. These percentage transmission measurements were then plotted on a semilogarithmic scale as a function of thickness. These plots may be interpreted from Lambert's law:

$$I = (1 - R)I_0 10^{-\alpha t}, \quad (1)$$

where I_0 and I are the intensities of the incident and transmitted radiation respectively, R is the reflection coefficient, and α is the absorption coefficient, which includes true absorption and body scattering. This relation can also be written in the following logarithmic form:

$$\log (I/I_0) = \log T = \log (1 - R) - \alpha t, \quad (2)$$

where T is the transmission. From Equation (2) it can be seen that a semi-logarithmic plot of transmission as a function of thickness should be a straight line if Lambert's law is obeyed; the negative slope is equal to the absorption coefficient, and the intercept on the $\log T$ axis gives a measure of the reflection coefficient.

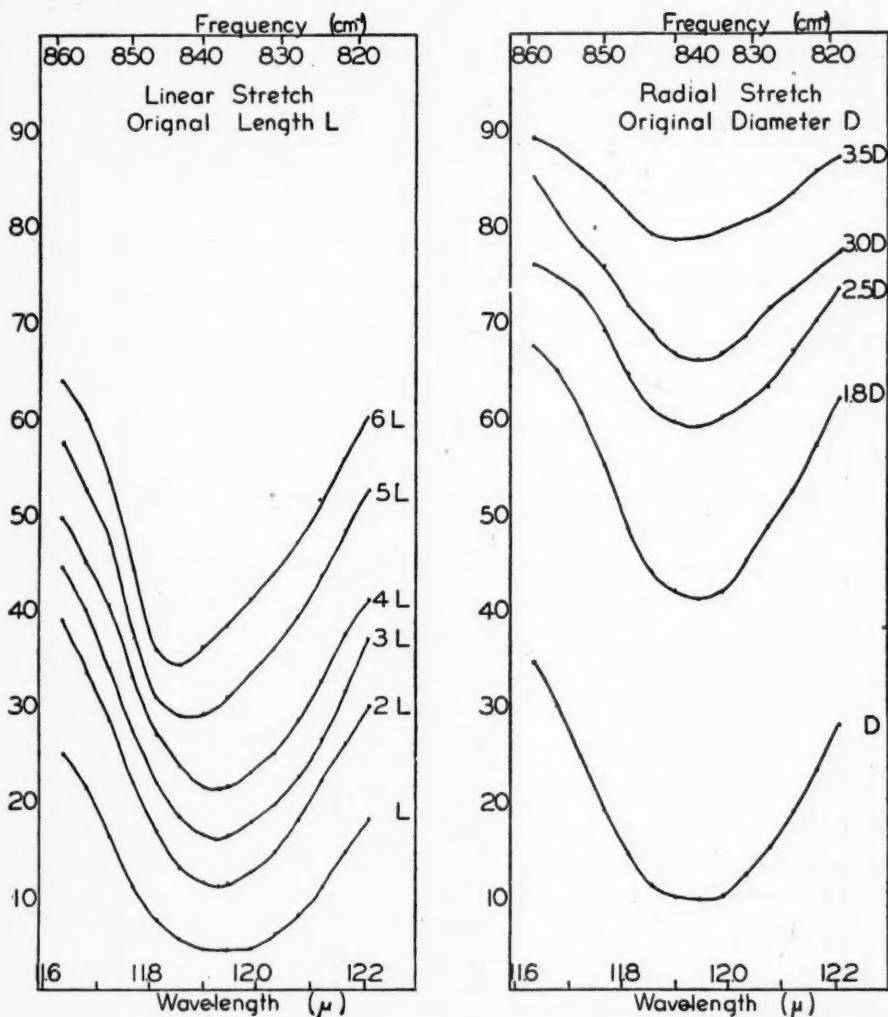


FIG. 2.—The transmission of rubber in the region of 11.9μ under various conditions of stretch.

It was found that the plots actually obtained were not straight lines even after the data had been corrected for stray radiation⁹. Typical plots for two bands are shown in Figure 3. The observed curvature can be explained if the absorption coefficient increases and the reflection coefficient decreases as the sample is stretched. The absorption coefficient at a given elongation can be

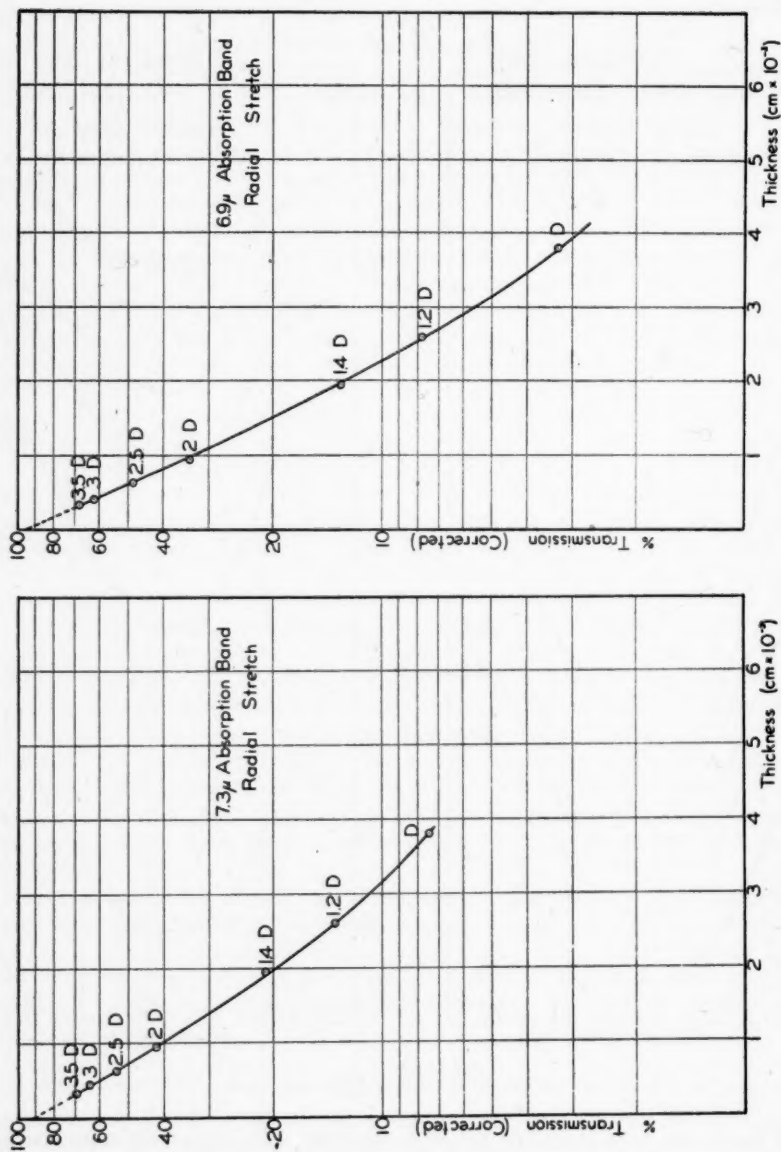


Fig. 3.—The effects of radial stretch on the transmission of rubber in the 6.9-μ and 7.3-μ regions. Transmission is plotted as a function of thickness; the conditions of stretch are indicated at the points on the curve.

obtained graphically by finding the slope of the tangent drawn at the appropriate point; the reflection coefficient can be determined from the intercept of the tangent. Whether the observed increase in the absorption coefficient is caused by an increase in true absorption or by an increase in body scattering cannot be determined, but the indications are that the increase is due to increased body scattering, since the plots for all bands studied show the same type of curvature.

Unfortunately the accuracy with which percentage transmission can be determined is only about 1 per cent. In the graphical determination of absorption coefficients, this inaccuracy introduces large errors when the transmission is low. Hence, the measured values of the absorption and reflection coefficients given in Table I for the strong absorption bands are not very

TABLE I

ABSORPTION AND REFLECTION COEFFICIENTS FOR CHARACTERISTIC ABSORPTION BANDS

Band	Absorption coefficient			Reflection coefficient		
	Un-stretched	Max. linear extension	Max. radial extension	Un-stretched	Max. linear stretch	Max. radial stretch
3.3 μ	...	$7.7 \times 10^2 \text{ cm}^{-1}$	$9.2 \times 10^2 \text{ cm}^{-1}$...	10%	10%
6.9	$3.6 \times 10^2 \text{ cm}^{-1}$	4.6	4.6	30%	9	6
7.3	2.6	3.6	3.3	34	9	12
11.9	2.4	2.6	2.8	20	5	6

* The sample was too thick for the determination of these coefficients.

accurate. For all bands studied the absorption coefficients increase and the reflection coefficients decrease with increasing stretch.

To estimate the part of the increased absorption arising from body scattering, measurements were made at various wave-lengths far from strong absorption bands. Typical results are shown in Figure 4. Since the transmission is high in these regions, the errors in the absorption coefficient produced by errors in transmission measurement are small. It will be seen from Figure 4 that the changes in both α and R are greatest at short wave-lengths, and become extremely small at long wave-lengths.

Figure 5 gives a graphical presentation of the observed changes in α as a function of wave-length, and Figure 6 shows the changes in R as a function of wave-length. Most of the points on these graphs fall near the smooth curves, except the changes in α for the bands at 6.9 μ and 7.3 μ . It is difficult to say whether the great changes at these wave-lengths are due to actual increases in true absorption or to experimental errors in determining the low transmissions at the center of these bands.

DISCUSSION OF RESULTS

A qualitative interpretation of the results of this study can be made in terms of the recent theories of rubber structure advanced by Wall¹⁰ and by James and Guth¹¹. From a consideration of the familiar properties of rubber, these authors conclude that, in the lightly vulcanized state, it consists of a coherent network of flexible hydrocarbon chains composed of independent C—C and C=C links of fixed length, with other molecules not actively involved in the network but acting like a fluid through which the network extends and in which the chains move with Brownian motion. It is estimated that approximately one-fourth of the molecules are involved in the network.

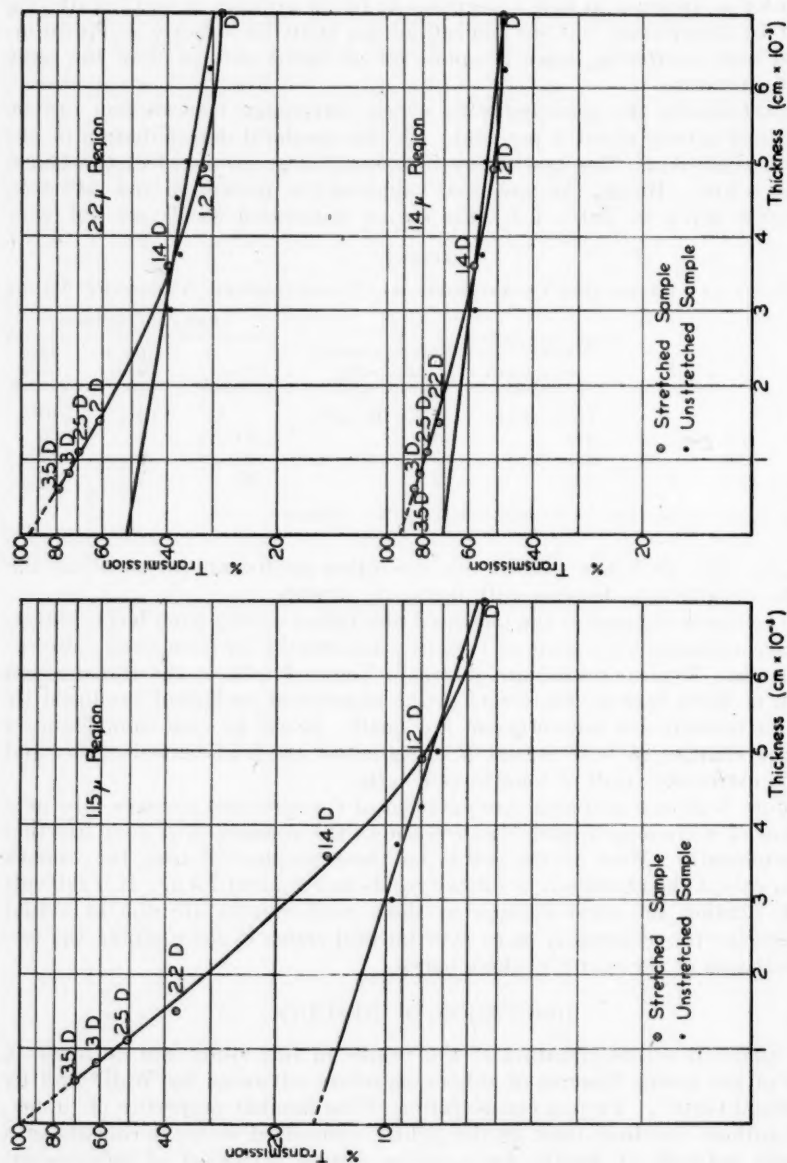


Fig. 4.—The effects of radial stretch on the transmission of rubber in regions remote from strong absorption bands. Transmission is plotted as a function of thickness; the conditions of stretch are indicated at the points on curve. The region indicated as 1.4μ at the center of part (b) should be 4.1μ instead.

According to James and Guth, the structural elements of rubber must be different from those of normal solids in which bonds of electrostatic, chemical, or van der Waals type connect atoms and molecules into a definite, rigid three-dimensional structure. The large extensibility suggests a more open type of structure. The small forces required to produce large extension in the early stages of stretch suggest that the elastic restoring forces cannot be of the types listed above, but may be explained in terms of flexible chains. Extensions to as much as four times the original length do not appreciably alter inter-atomic distances in the chains. Only for large extensions at which rubber begins to crystallize or approaches the breaking point do the chemical bonds between carbon atoms come into play. However, at maximum extension these chemical bonds do appear to contribute to the tensile strength of rubber, which

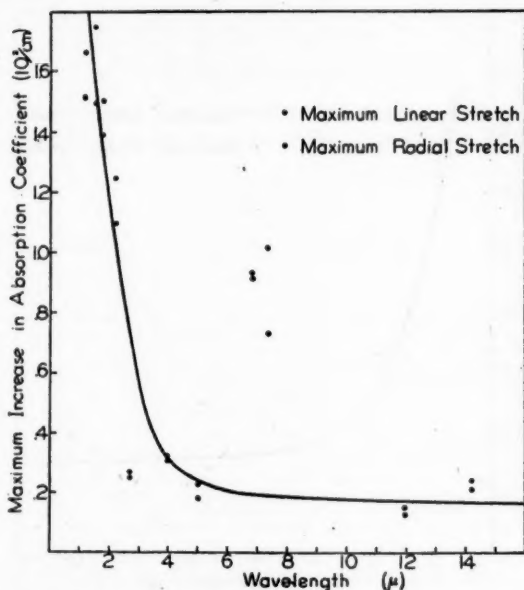


Fig. 5.—The increase in the absorption coefficient of rubber produced by stretching. The increases are plotted as a function of wave-length.

(if computed with respect to the cross-section at the breaking point) is almost equal to that of copper.

Upward curvature of the stress-strain curve for the rubber used in the present work sets in when the length of the sample is approximately four times the original length. This curvature is explained according to James' theory as due to the gradual approach of the molecular network to its maximum extension, which for the material used was six and one-half times its length in the unstretched state. It will be recalled that, for extensions above four times the original length, the band near 11.9μ began to shift toward shorter wavelengths. This band has been observed in the spectra of many hydrocarbons, and has been attributed to the fundamental vibration of the C—C group. Hence, the observed changes can be interpreted as arising from changes in the characteristic frequency of this group. These changes set in at the stage of

extension where strains would be expected to begin in the individual links in the hydrocarbon chain. The asymmetrical shape of the band may possibly be caused by the fact that the C—C groups in molecules not involved in the network are subjected to stresses of a different type from that experienced by the C—C groups in the network; hence their vibrational frequencies would probably be different. The existence of slightly different C—C frequencies would generally produce an asymmetrical absorption band. As no changes were observed in the 6- μ region where the C=C group has an absorption band, it is concluded that the effects of strains on this group are not as great as in the case of the C—C group.

The observed increases in the absorption coefficient can be explained as arising from scattering by the crystalline lattices formed when maximum

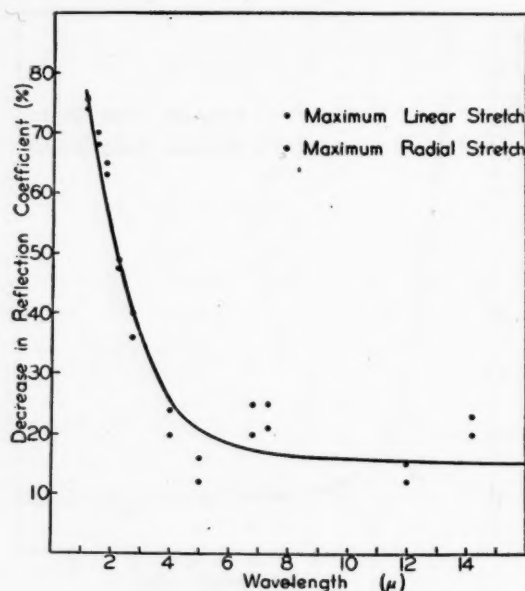


Fig. 6.—The decrease in the reflection coefficient of rubber produced by stretching. The decreases are plotted as a function of wave-length.

elongation is approached. The observed relationship between change in absorption coefficient and wave-length would tend to support this interpretation. Scattering by these crystal lattices would be of the type treated by Einstein¹² in his theory of scattering in dense media. From this relation the average crystal size could be calculated from the data obtained if the refractive indices of the crystal and matrix material were known. It would be interesting to test the hypothesis of scattering by crystals by measuring the transmission of stretched samples of synthetic rubber substitutes. Some of these show evidence of crystallization and others do not. The only indications of a change in true absorption were in the 6.9- and 7.3- μ bands. It is felt that this observed effect is probably due to experimental error in determining transmissions at the bottom of these strong bands or in an error in the correction for stray radiation.

The decreases in reflection coefficient are readily explained as being due to decreases in surface irregularities accompanying stretch. The variation of this change with wave-length is in agreement with this explanation and observation of the reflection of visible light at various angles of incidence affords additional confirmation.

SUMMARY

The transmission spectrum of natural rubber has been studied in the region between 1μ and 15μ and the effects of linear and radial stretch have been observed. Linear extension greater than 400 per cent of the original length produces an increase in the C—C vibrational frequency. Both linear and radial stretch produce an increase in absorption coefficient and a decrease in reflection coefficient. The changes in absorption and reflection coefficients are greatest at short wave-lengths.

ACKNOWLEDGMENT

The writers wish to express their appreciation to J. Rud Nielsen for his criticism of the manuscript and to (Miss) Annette Herald for the preparation of the figures.

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- ⁹ The corrected percentage transmission T was obtained from the observed percentage transmission T' by means of the following relation: $T = T'(C_1 - C_0T')$, where C_1 is the percentage of stray radiation in the incident beam. The relation holds for small values of C_1 and C_0 . The magnitudes of the corrections were obtained by measuring the percentage transmission at the flat bottoms of absorption bands produced by samples so thick that true transmission was negligible. Thick rubber samples were used to find C_1 and thick cells containing hydrocarbons were used to determine C_0 . This value of C_0 is not an exact measure of the total stray radiation, but the values are applicable, since rubber is a hydrocarbon.
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THE X-RAY DIAGRAM OF A BUNA-S VULCANIZATE *

ROSS E. MORRIS AND CHARLES B. JORDAN

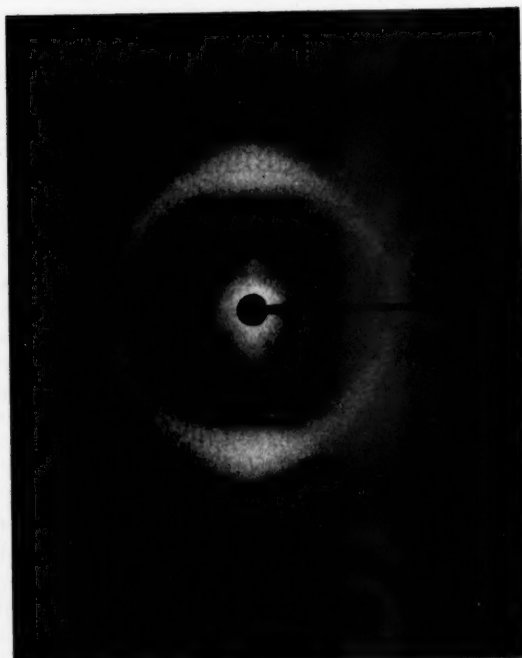
RUBBER LABORATORY, U. S. NAVY YARD, MARE ISLAND, CALIFORNIA

Sebrell and Dinsmore (*India Rubber World* 103, 37 (1944); *RUBBER CHEM. TECH.* 16, 857 (1943)) found that the x-ray diffraction pattern of Buna-S consists of a broad halo similar to that obtained with liquids. This type of pattern was obtained whether the Buna-S was unstretched or stretched. Unstretched natural rubber gives a similar pattern, but stretched natural rubber gives a characteristic fiber pattern. This fiber pattern demonstrates the existence of three-dimensional crystallites.

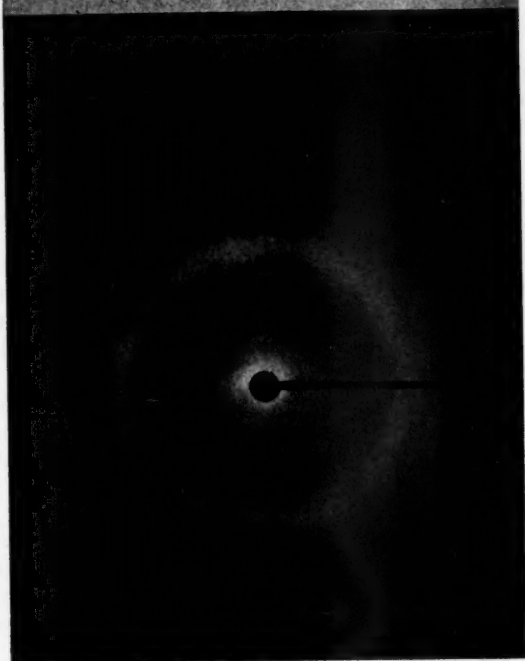
Buna-S would not be expected to yield a fiber diagram while stretched because the molecules of this synthetic rubber are probably not constructed in a regular fashion. The styrene residues are presumably distributed at random along the length of the molecule, and there may be side-chains which branch off the main chain. However, when considerably stretched, a Buna-S vulcanizate would be expected to exhibit some indication in its x-ray diagram that alignment of the molecules has occurred.

The authors have obtained evidence that the molecules of Buna-S do line up together when considerably stretched. By stretching a specimen of Buna-S tread vulcanizate to 500 per cent elongation and exposing it for 40 minutes to x-rays, the diagram shown below was obtained. For comparison the x-ray diagram of the unstretched Buna-S vulcanizate is given. It will be noted that the halo in the case of the stretched specimen has split into two arcs. A similar phenomenon was observed for a stretched Buna-N tread stock by Sebrell and Dinsmore, who interpreted it to mean a high degree of alignment of the chain molecules in the direction of stretching without the formation of a three-dimensional lattice.

* Reprinted from *The Rubber Age* (N. Y.), Vol. 55, No. 2, page 161, May 1944.



Stretched 500 per cent



Unstretched

TWO MODES OF ACTION OF ANTIOXIDANTS IN RUBBER *

JEAN LE BRAS

It is a commonly accepted belief that antioxidants protect oxidizable products from the harmful effects of oxygen by retarding the rate at which these oxidizable products combine with oxygen. Consequently, if the oxidizability of a rubber mixture containing no antioxidant and the oxidizability of the same mixture to which such an agent has been added are measured under the same conditions, the absorption of oxygen would be expected to be distinctly less rapid in the second case. This has, in fact, been proved to be true in general, not only for rubber, but also for other substances which are protected by antioxidants.

In a systematic study of a series of antioxidants of differing chemical compositions, various observations were made which gave indications that these products react in two different ways. In these experiments a rubber mixture of chosen composition was prepared as a blank or control, and was compared with other mixtures of the same base composition to which various antioxidants selected for study had been added in the same proportion in all cases.

The oxidizability of all these mixtures and the curves of their decreases in tensile strength in a 70° air-oven were then determined¹. In this way it was proved that some antioxidants reduce considerably the rate of combination of oxygen with rubber, in some cases to a third or quarter of the rate in their absence. On the contrary, although having a protective effect as judged by deterioration in the 70° air-oven, other antioxidants reduce the rate of oxidation to only a slight degree.

It appears, therefore, that antioxidants have two different modes of action, which can be explained in the following way. Substances belonging to the first type inhibit, in accord with the normal mechanism of antioxygenic action², and in proportion to their activity, the combination of oxygen with rubber. However, in this case, any oxygen which escapes this protective action then forms peroxides, which in turn bring about profound deterioration of the rubber just as happens in mixtures not so protected.

Substances of the second type do not retard the combination of oxygen with rubber; their function is instead to deactivate the peroxides by transforming them into oxides of rubber, which have only relatively little deleterious effect³. This view, as would be expected, is in perfect accord with the doctrine of autooxidation⁴.

These two mechanisms are represented by two ideal types of protective agents, which are characterized by the fact that in the case of true *antioxygenic substances* the deterioration of rubber when a given proportion of oxygen is absorbed⁵ is the same whether or not the agent is present, whereas in the case

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Comptes Rendus hebdomadaires des séances de l'académie des sciences*, Vol. 217, No. 13, pages 297-299, September 27, 1943.

of *deactivating substances*, there is no deterioration, at least theoretically, when a deactivating substance is present.

From the practical point of view, each protective agent apparently tends to react by both mechanisms, with one or the other of the two mechanisms more or less the controlling effect. As examples of the two types, phenyl- β -naphthylamine tends to react as an antioxygenic substance, whereas mercaptobenzoimidazole tends to react as a deactivating agent. Phenyl- β -naphthylamine retards the oxidation of rubber but reduces to only a slight extent the harmful effects of oxygen, *e.g.*, for a given percentage of oxygen absorbed, deterioration is but little less than that of the same mixture containing no such agent. On the other hand, mercaptobenzoimidazole reduces considerably the harmful effect of oxygen, yet retards oxidation to only a slight extent.

The mechanisms of the reactions of these two compounds differ sufficiently to make it seem possible, by combining their effects, to obtain a considerable increase in protective power. With this in view, three mixtures were tested in comparison with the blank mixture: (1) the blank mixture to which 2 parts of phenyl- β -naphthylamine had been added; (2) the blank mixture to which 2 parts of mercaptobenzoimidazole had been added, and (3) the blank mixture to which 1 part of phenyl- β -naphthylamine and 1 part of mercaptobenzoimidazole had been added.

On aging 36 days in an air-oven at 70° C, the mixture to which no agent had been added lost 94 per cent of its original tensile strength, the mixture containing 2 parts of phenyl- β -naphthylamine lost 51 per cent of its original strength, the mixture containing 2 parts of mercaptobenzoimidazole lost 33 per cent of its original strength, and the mixture containing 1 part of phenyl- β -naphthylamine and 1 part of mercaptobenzoimidazole lost only 6.5 per cent of its original strength.

The protective effect which can be obtained in this way by mixtures of two different types of antioxidants is remarkable, and the experimental results confirm in a striking way what might be predicted on a theoretical basis.

This method of investigation makes it possible, therefore, to select on a rational basis mixtures of antioxidants which will show a high degree of effectiveness.

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- ² Dufraisse, *Rev. gén. caoutchouc* 9, Nos. 85 and 87 (1932); "The Chemistry and Technology of Rubber", Edited by Davis and Blake, Reinhold Publishing Corp., New York, 1937, p. 440.
- ³ An isolated fact has been observed in the case of litharge, which from the point of view of oxidizability, seems to function as a prooxygenic agent (cf. Dufraisse, Drisch and Pradier-Gibello, *Rev. gén. caoutchouc* 10 (1933); *RUBBER CHEM. TECH.* 7, 167 (1934).
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- ⁵ It should be understood that in this case only incipient oxidation is in question (in this connection, see for example, Dufraisse, "Traité de Chimie Organique de Grignard", 1936, Vol. 2, p. 1147).

REACTIONS OF IODINE, IODINE CHLORIDE AND THIOCYANOGEN WITH THE HYDROCAR- BONS OF NATURAL RUBBER AND SYNTHETIC RUBBER *

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Studies of the reactions of halogens with the hydrocarbons of rubber, balata and gutta-percha have made it possible to determine the unsaturation of rubber and analogous substances and to verify certain concepts of the structure of these high-molecular compounds. The reactions of these hydrocarbons with chlorine, bromine and iodine chloride have been studied in particular detail¹.

Chlorinated rubber, which has particularly valuable technical properties, has already found practical applications. Also it has been found possible to utilize the reaction of bromine in analytical procedures and in the preparation of other derivatives of rubber, such as dyes of high molecular weight and other compounds of importance.

Work by various investigators has established the fact that the reactions of rubber with chlorine and with bromine do not proceed simply, but involve substitution reactions. The reaction of rubber with iodine is complicated by secondary reactions. Weber², one of the first investigators to study this reaction, described an iodine derivative of the hydrocarbon of natural rubber, analysis of which corresponded to the composition, $C_{20}H_{32}I_6$.

However, it has been found that the results are not always reproducible. For example, Hinrichsen and Kemp³ observed important oxidation reactions. Reformatsky⁴ in an investigation of the properties of Russian plants (kondrilla, tau-saghyz and others) obtained products containing different iodine contents. Kemp and Mueller⁵, Fisher and McCollm⁶, and others found that the reactions of rubber, gutta-percha and thermoprene with iodine are extremely slow.

Thanks to the work of Kemp and Mueller, the reaction of iodine chloride has become of great significance at the present time. In a study of the reactions of various halogen compounds, Kemp⁷ showed that iodine chloride has certain advantages over bromine in its reaction with high-molecular compounds. In its reaction with cold solutions of natural rubber and gutta-percha in carbon disulfide, iodine chloride adds quantitatively, gives theoretically correct iodine numbers, and therefore is recommended by Kemp for the quantitative determination of the hydrocarbons of rubber, gutta-percha and similar natural products. This method was elaborated in considerable detail by Kemp and Mueller in 1934⁸.

The reaction with iodine chloride was used by Pummerer⁹ for studying the chemical characteristics of sol and gel rubber, and also for determining the

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iodine numbers of crude rubber. Pummerer studied these reactions in chloroform and in carbon tetrachloride. In this way he confirmed the results obtained by Kemp and acknowledged the excellence of the method. The results obtained by Kemp were verified also by Kheraskova and Korsunskaya⁹. The method of Kemp has been used with success by many investigators for determining the purity of rubber, for the direct determination of the hydrocarbon in weakly vulcanized rubber¹⁰ and also for determining differences in the hydrocarbons of rubber, balata and gutta-percha which are brought about by different methods of processing¹¹. Less reliable results are obtained in determining the iodine numbers of natural rubber and of gutta-percha by the use of iodine bromide¹².

As in the case of halogens, studies of the reactions of free thiocyanogen, which has become available in the last two decades, have led to results of great interest. It is well known that thiocyanogen has properties analogous to those of the halogens. Free thiocyanogen is now widely used in organic syntheses. The patent literature cites the use of thiocyanogen in the cold vulcanization of rubber.

According to investigations by Kaufmann¹⁴, thiocyanogen gives stable solutions in anhydrous carbon tetrachloride and in glacial acetic acid. Kaufman used these solutions successfully in investigations of oils and fats, developed the science of thiocyanogenometry, and introduced a new constant—the thiocyanogen number. In connection with this subject, Pummerer and Stärk¹⁵ endeavored to use thiocyanogen for the direct determination of rubber hydrocarbon. They found that the reaction of relatively concentrated solutions of natural (NK) rubber and thiocyanogen at 0° C gave a theoretical yield of a substance of the composition corresponding to the empirical formula, $C_5H_8(SCN)_2$. Nevertheless the thiocyanogenometric method for determining the iodine numbers of rubber has no advantage over the iodine chloride method. The various investigators used natural products in most cases. At that time these reactions had not been applied to synthetic rubbers, or at least no such experiments are described in the literature.

In the present paper, some results obtained in experiments on the reactions of iodine, iodine chloride and thiocyanogen with sodium-butadiene (SK) rubber, which is used so widely in Russia, are described. Although we have not succeeded in demonstrating that it is possible to apply these reagents to the quantitative determination of the hydrocarbon of SK rubber, the data which have been obtained may be useful in characterizing SK rubber chemically, and in making it possible to estimate the composition and define the properties of the reaction products.

Most of this work was repeated with NK rubber. A comparison of the experimental results shows that NK rubber and SK rubber behave similarly in these reactions, although, because of structural differences, SK rubber shows less activity than NK rubber.

EXPERIMENTAL PART

The original samples of hydrocarbons which were studied were prepared by the following method. The synthetic rubber was prepared by polymerization of technical butadiene in the presence of sodium wire in a sealed ampoule, which was let stand for about six months. The hydrocarbon was then extracted with benzene, and the rubber was precipitated from this benzene solution by alcohol. The isolated product was dried in a current of carbon

dioxide and in a vacuum desiccator at room temperature to constant weight. The product was colorless, transparent, and elastic. Pure NK hydrocarbon was prepared from smoked sheet. Finely divided particles of smoked sheet rubber were purified by first washing with a dilute solution of sodium hydroxide and water, drying, and extracting with acetone in a van der Vrienderik extractor until a test indicated the absence of resins. The rubber was finally purified by dissolving it in chloroform and precipitating it with alcohol three times. After being purified in this way, the hydrocarbon was dried in the same way as SK rubber. The product was transparent, slightly yellowish, viscous, and elastic, gave no reaction for nitrogen, and contained no inorganic components.

In carrying out the reactions of these hydrocarbons, the experimental conditions were kept as nearly as possible the same. In the following pages the experiments are described, and the results obtained are recorded.

THE REACTION OF SK HYDROCARBON WITH IODINE

The reaction was carried out with iodine which had first been sublimed for the purpose.

A one-gram sample of SK hydrocarbon was dissolved in 25 milligrams of carbon tetrachloride, and allowed to stand overnight in a flask which was filled with carbon dioxide and closed with a ground glass stopper. A saturated solution of iodine in carbon tetrachloride was added in 100 per cent excess. After allowing the mixture to stand, the unreacted iodine was titrated with 0.1 *N* normal sodium thiosulfate, with the addition of 0.5 per cent starch solution as the indicator. At the same time a control titration of an iodine solution was carried out, and from the difference in the results the iodine number of the SK hydrocarbon was calculated.

It was found that the reaction of SK hydrocarbon with iodine proceeds very slowly in darkness; consequently this reaction in darkness was not investigated thoroughly. The iodine number, determined 48 hours after the beginning of the reaction at 17° C, deviated 6 per cent from the theoretical value of 469.6° C. The reaction was considerably accelerated when the flask containing the mixture was exposed to diffused light or still more so when it was exposed to direct sunlight. Thus in one series of experiments the absorption of iodine (addition and substitution) was 50 to 60 per cent of the theoretical value (without corrections) after 2-3 days at room temperature.

THE REACTIONS OF NK AND SK HYDROCARBONS IN SOLUTION

In darkness the reaction of the hydrocarbons with iodine chloride proceeds more energetically than with iodine. The experimental procedure was approximately the same as that used in previous experiments. A sample of about 0.1 gram of hydrocarbon was dissolved in 25 milligrams of anhydrous carbon tetrachloride saturated with carbon dioxide, and allowed to stand overnight, after which 100 per cent excess of 0.2 *N* iodine chloride in glacial acetic acid was added. The reaction mixture was agitated continuously by rotating the flask. Before titration of the unreacted iodine chloride with sodium thiosulfate, 10 milligrams of a 15 per cent aqueous solution of chemically pure potassium iodide was added and, before completion of the titration, starch solution was added.

When Wijs solution was added to a solution of rubber, coagulation took place immediately, with formation of light pink-violet flocculates. Notwith-

standing the fact that the reaction with iodine chloride proceeded rapidly, it was subsequently retarded by this coagulation, and therefore it was impossible to follow the reaction as well as could have been done in a homogeneous system. The visible phenomena in these experiments with NK and SK hydrocarbons were similar to those observed by Pummerer. The method of Kemp is obviously superior to this, because he recommends the use of carbon disulfide as a solvent for rubber, in which case there is no coagulation of the reaction product.

If the combination of iodine chloride with the rubber hydrocarbons takes place quantitatively, in complete agreement with the theory, *i.e.*, if one molecule of iodine chloride combines with each C_6H_5 group in the NK hydrocarbon and with each C_4H_9 group in SK hydrocarbon, then their unsaturation values are equivalent to their theoretical iodine numbers, *viz.*, 372.9 for NK hydrocarbon and 469.6 for SK hydrocarbon.

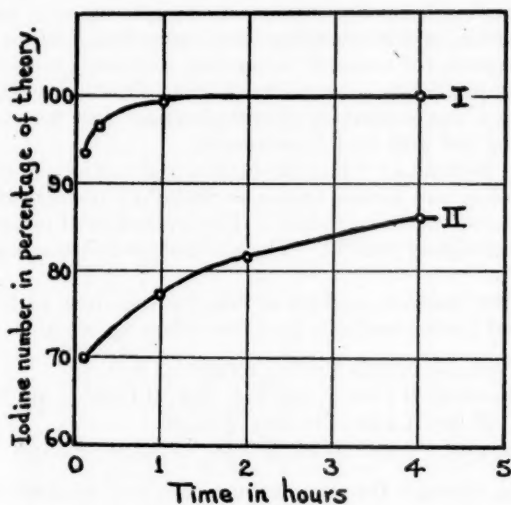


FIG. 1

Determination of the iodine numbers of NK hydrocarbon by iodine chloride when the reaction was carried out at $0^\circ C$ for 5, 15, 60 and 240 minutes gave values of 93.3, 97.0, 99.5 and 100.6 per cent, respectively, of the theoretical value. Analogously, with SK hydrocarbon at the same temperature for 5, 60, 120 and 240 minutes, the iodine numbers were found to be 69.9, 77.1, 81.5, and 86.3 per cent, respectively, of the theoretical value. At higher temperatures a higher proportion of iodine chloride reacted. In one case the iodine numbers of SK hydrocarbon at room temperature ($15-16^\circ C$) 39.5 hours after the beginning of the reaction was 104.3 per cent of the theoretical value. The results obtained with NK hydrocarbon agreed with data already published.

Under the conditions described, the reactions with iodine chloride proceed rapidly at first (see Fig. 1), then become slower, probably because from this point on the reactions involve chiefly adsorption and substitution.

The reaction of NK hydrocarbon with iodine chloride proceeds to completion in 1-1.5 hours. In the case of SK hydrocarbon, the reaction with iodine chloride proceeded at first rapidly and then, after having become 80-85 per

cent complete in 3-4 hours, became slower. Only after 30-40 hours did the iodine number reach the theoretical value. This fact makes it impossible to use the iodine chloride method for determining SK hydrocarbon, at least under the conditions described, and for determining SK hydrocarbon, bromine seems to be more satisfactory.

In studying the products of these reactions the same conditions were followed, but larger quantities of the reagents were used. From the reaction product of NK hydrocarbon obtained after 1 hour's reaction and from the product obtained from SK hydrocarbon after 30 hours' reaction, products were isolated which have not been previously described in the literature. They were at first pinkish-violet, but after washing with alcohol and ether were finally obtained in the form of white amorphous solids with densities ranging from 2 to 3. Both products were insoluble in ethers, ketones, alcohols and phenol; swelled slightly in aromatic hydrocarbons; swelled more in halogenated derivatives, for example, in dichlorethane, chloroform, etc.; and swelled considerably in aniline, dimethylaniline, and quinoline. When warmed with amines, they reacted; for example, when the addition product of SK hydrocarbon and iodine chloride was warmed with dimethylaniline, the product which was formed was soluble in dimethylaniline, and was manifest by the solution becoming red with blue fluorescence.

The addition product of NK hydrocarbon and iodine chloride became soft at 74-76° C, swelled and turned brown at 88-90° C, turned black at 90-95° C and began to evolve vapors of iodine. This evolution of iodine reached completion at approximately 345° C. The residue on the cooling surface was a viscous substance.

Analysis of the reaction product of NK hydrocarbon with iodine chloride by the Liebig and Carius methods gave the following results:

0.1166 g. substance: 0.1184 g. CO₂; 0.0376 g. H₂O
0.0988 g. substance: 0.1554 g. AgCl + AgI; 0.1176 g. AgCl
found (%): C 27.69; H 3.61; Cl 14.61; I 53.09
C₅H₈ClI computed (%): C 26.04; H 3.50; Cl 15.38; I 55.08

When heated through the temperature range of 95-240° C, the reaction product of SK hydrocarbon with iodine chloride likewise decomposed, with evolution of iodine and carbonization. The product remaining after liberation of all iodine was a viscous asphalt-like mass.

Analysis of the reaction product of SK hydrocarbon with iodine chloride gave the following results:

0.1048 g. substance: 0.0888 g. CO₂; 0.0334 g. H₂O
0.1254 g. substance: 0.2096 g. AgCl + AgI; 0.1586 g. AgCl
found (%): C 23.07; H 3.57; Cl 15.52; I 56.45
C₄H₆ClI computed (%): C 22.18; H 2.80; Cl 16.38; I 58.64

Analyses of these two products showed that the reactions of both natural and synthetic rubber hydrocarbons involve the addition of whole molecules of iodine chloride at the double bonds of the hydrocarbons, with formation of polyiodochloride derivatives. The yields of the products were almost quantitative. The deficient halogen contents of the reaction products can perhaps be explained in part by the formation of hydrogen halides, which were not determined in the present work, and in part by oxidation reactions which could not be entirely prevented.

The products which were obtained may be of interest in the synthesis of other more complex derivatives of rubber by means of substitution reactions.

THE EFFECT OF THIOCYANOGEN ON NK AND SK HYDROCARBONS

To study these reactions, a 0.2 N solution of thiocyanogen in carbon tetrachloride (dried and distilled over phosphorus pentoxide) was used. The thiocyanogen was prepared in the usual way, *i.e.*, by the action of bromine on a fine suspension of potassium thiocyanate in carbon tetrachloride, and the solutions of the rubber hydrocarbons were prepared as already described. The thiocyanogen reactions were carried out at room temperature (16–17° C). To each rubber solution was added the customary excess of thiocyanogen solution and, after predetermined periods of time, the unreacted thiocyanogen was titrated with sodium thiosulfate in the presence of aqueous potassium iodide and starch.

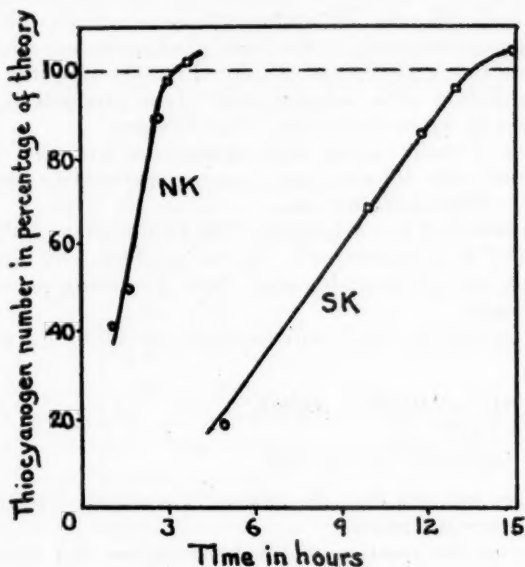


FIG. 2

No visible changes were observed at first in the reaction mixture of NK hydrocarbon and thiocyanogen, but after about 15 minutes gelation took place, followed by syneresis. This is in complete agreement with the experiments of Pummerer. It is most convenient to carry out the titration of the unreacted thiocyanogen at this point. The theoretical value of NK hydrocarbon is 170.6. The experimental thiocyanogen values were calculated by deducting the values obtained in control experiments. Thus after 70, 100, 160, 180 and 220 minutes, the thiocyanogen numbers were found to be 41.8, 50.9, 88.8, 98.6 and 102.2 per cent of the theoretical values.

During the reaction of thiocyanogen with SK hydrocarbon, gelation did not set in until later, and syneresis was complete only after a long time. As a result, titration by sodium thiosulfate was made difficult because of the formation during agitation of a rather stable foam, which hampered a reading of the

end point of the titration. The theoretical thiocyanogen number of SK hydrocarbon was 214.9. The thiocyanogen numbers, determined after 4.5, 10, 12, 13 and 15 hours, were 20.1, 68.6, 86.1, 95.3 and 104.3 per cent, respectively, of the theoretical value. The results obtained in the determination of the thiocyanogen numbers of both hydrocarbons are shown in Figure 2, which makes evident the abnormality in the absorption of thiocyanogen by SK in the initial stage of the reaction, during gelation, and subsequent occurrence of syneresis. Furthermore, neither curve in Figure 2 shows any evidence of a well-defined end point in the reaction with thiocyanogen, evidently because of polymerization of thiocyanogen and other secondary processes.

At a certain point in the course of the reaction an orange or carrot color appeared. This is explained by the adsorption of pseudo-thiocyanogen, which was greater in the reaction with NK hydrocarbon than it is with SK.

The products of these reactions are best isolated by the addition, at the end of the reaction, of alcohol or acetone to the reaction mixtures. The products from both SK and NK hydrocarbons were hard, brittle amorphous substances, and were recovered in the form of white masses when the times of the reaction were short, and as carrot-colored masses when the reactions were prolonged. Extraction with acetone made these products lighter in color, evidently because of removal of pseudo-thiocyanogen.

The densities of these various hard products of the reactions of SK and NK hydrocarbons with thiocyanogen were approximately the same as the density of liquid carbon tetrachloride.

When the product of the reaction of NK hydrocarbon with thiocyanogen was heated to 150° C, it carbonized. It was unaffected by most solvents except aniline and carbon disulfide, which had a swelling action. It gave a reaction for nitrogen.

Analysis according to the Carius method on sulfur gave the following results:

0.1402 g. substance: 0.3551 g. BaSO₄
found (%): S 34.79
C₅H₈(SCN)₂ computed (%): S 34.81

These analyses indicate that the product was identical to the product obtained by Pummerer and Stärk.

The product of the reaction of SK hydrocarbon and thiocyanogen carbonized at approximately 190° C. Most solvents had no effect on it; however, it swelled strongly in aniline and carbon disulfide, as did the reaction product of NK hydrocarbon and thiocyanogen.

Analyses of one of the samples obtained in this reaction gave the following results:

0.1194 g. substance: 0.1840 g. CO₂; 0.0366 g. H₂O
0.1203 g. substance: 17.2 mg. N₂ (20°, 754.6 mm.)
0.1124 g. substance: 0.3132 g. BaSO₄
found (%): C 42.03; H 3.42; N 16.16; S 38.27
C₄H₆(SCN)₂ computed (%): C 42.31; H 3.55; N 16.46; S 37.68

These data indicate that the thiocyanogenation of SK hydrocarbon leads to the formation of a polythiocyanate of this hydrocarbon. It is obvious that there is a complete analogy between the behavior of the hydrocarbons of natural and synthetic rubber in their reactions with thiocyanogen. At the

same time, the reactions of these two hydrocarbons show the peculiarities which are attributable to the characteristic structures of their double bonds, particularly the influence of methyl groups attached to carbon atoms having double bonds in the case of NK hydrocarbon, and the absence of this influence in the case of SK hydrocarbon.

The polythiocyanates which are obtained in this work suggest the possibility of obtaining from them, by dry distillation and oxidation, a new series of hitherto unknown products, which will aid in explaining the structure of rubber and the nature of vulcanization.

SUMMARY

The reactions of iodine, iodine chloride and thiocyanogen with solutions of natural rubber and of synthetic sodium-butadiene rubber were studied.

The experimental results show that the chemical properties of these two hydrocarbons are in general similar, although there are also certain differences which can be explained by the peculiarities of their structures.

The products of the reactions of iodine chloride and of thiocyanogen with natural rubber and sodium-butadiene rubber were isolated, and their compositions and some of their properties are described.

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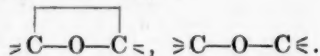
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DISTRIBUTION OF OXYGEN IN OXIDIZED RUBBERS *

RALPH F. NAYLOR

It has been fairly well established that the initial products of the auto-oxidation of polyisoprenes are hydroperoxides¹. The course of subsequent reactions is not, however, so clear. Under normal conditions the peroxides are unstable, and give rise to a large variety of secondary oxidation products. The object of the present work is to study the distribution of oxygen in the various groups which have resulted from these secondary reactions.

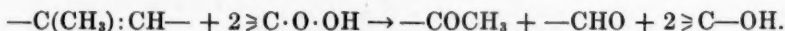
The course of oxidation.—Oxidative fission of the double bond of an isoprene unit may be expected normally to give rise to a carbonyl and an aldehyde group, and the latter may be further oxidized to carboxyl. The hydroperoxide groups which effect this oxidation are, as experience shows, mainly reduced to alcohol groups. Epoxides may result from transference of the active oxygen from the peroxide groups to the olefinic bonds, and esters and ethers by subsequent reactions of the alcoholic groups. Thus any or all of the following functional groups may be expected to be present in an oxidized rubber:



The oxidized rubbers.—The only complete examination which has so far been carried out on the distribution of oxygen in these groups in oxidized rubber is that of Hilton², who worked with a fraction of commercial oxidized rubber (Rubbone-B) which contained about 10 per cent oxygen. This material is produced by prolonged mastication of rubber in the presence of air, cobalt naphthenate and cellulosic material³, the total product being normally separated into three fractions, C, B and A, by successive extraction with methylated spirits and acetone. Thus Rubbone-C is the first extract with methylated spirit; Rubbone-B is the subsequent extract with acetone; and Rubbone-A is the residue after extraction. To study the effect of the extent of oxidation on the oxygen distribution, it was decided to examine Rubbone-C, a heavily oxidized rubber (13 per cent oxygen), and nitrite crumb rubber, which contains only 2 per cent oxygen, and to compare the results with those of the intermediate Rubbone-B. Commercial nitrite crumb rubber is obtained by incorporating a small amount of sodium nitrite in latex before coagulating it with acetic acid⁴. The liberated nitrous acid effects a mild oxidation of the rubber, which is probably due partly to introduction of nitroso groups, but mainly to aerial oxidation. In addition to these materials, D. A. Sutton kindly supplied three samples of autooxidized rubber which had been prepared in the presence of boiling phenol. These samples (P₁, P₂ and P₃) contained 3, 5 and 10 per cent oxygen, respectively, and the oxygen distribution is quoted below for purposes of comparison.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 20, No. 2, pages 45-53, August 1944.

The products of oxidative fission.—Oxidation of rubber involves a breakdown of the molecule into smaller fragments, the sizes of which may be compared by the viscosity method of molecular weight determination. In the most oxidized product, Rubbone-C, the molecular weight has been reduced from 300,000 to 2,400, with the introduction of 13 per cent oxygen. If it is assumed that the oxidative agent is the hydroperoxide group, and that the molecule is broken in the simplest way, *i.e.*, by the fission of a double bond to give an aldehyde and a ketone, then stoichimetrically, four oxygen atoms as a minimum will be associated with every fission.



Thus each molecule of Rubbone-C, whose molecular weight is 2,400, will contain 2.7 per cent oxygen directly associated with the fission reactions. Even if allowance is made for the subsequent oxidation of the aldehydic group to a carboxylic acid, the total oxygen requirement is only 4 per cent. It follows, therefore, that a large amount of oxygen must be utilized either in oxidizing methyl groups, *e.g.*, to carboxyl, or in saturating some of the unsevered olefinic bonds. Extensive reaction of the former type would involve an increase of the C/H ratio, but in fact the ratio for Rubbone-C is slightly lower than that for rubber; the same is true for Rubbone-B and nitrite crumb; only in the products P₁, P₂ and P₃ is a higher C/H ratio to be observed, and here the increase is probably due to the incorporation of phenol into the rubber molecule. Moreover, the unsaturation of the original rubber is found to be continuously reduced as the result of oxidation, and it will be shown that the amount of that reduction corresponds to the introduction of one atom of oxygen to each double bond which has become saturated. Confirmation of the view that phenol has entered the molecule of the product P₃ is provided by the fact that P₃ is slightly more saturated than Rubbone-C (iodine values 250 and 260, respectively), although its oxygen content and its degree of degradation are both smaller than those of Rubbone-C (molecular weights 4,000 and 2,400, respectively).

Determination of the molecular weight of nitrite crumb is rendered difficult by the fact that it is insoluble in all the usual rubber solvents. It is possible to obtain a 2 per cent solution by heating the rubber with xylene for 1½ to 2 hours, at 120–140° C, and using this solution for molecular weight determination a value of 72,000 was obtained. On removing in a high vacuum the solvent from a portion of this solution, a sticky yellow product is obtained, and this is completely soluble in benzene. It is evident, therefore, that degradation of the nitrite crumb has occurred, and the figure 72,000 must be too low. The physical character of the original rubber would suggest a molecular weight of more than double this value.

Analytical methods.—For estimation of the peroxidic oxygen content of the oxidized rubbers, the colorimetric method of Bolland, Sundralingam, Sutton and Tristram⁵, depending on the oxidation of colorless ferrous thiocyanate to the red ferric salt, was adopted. Direct titration with alkali gave the acid value, and saponification with hot alcoholic alkali, the sum of all the oxygen contained in acidic and ester groups. It was assumed that this oxygen was present in carboxyl and carbalkoxyl groups. For determining small active hydrogen values, Bolland⁶ developed an accurate method by adapting the Zerewitinoff determination to high-vacuum technique, and essentially this method was used for the present work. The active hydrogen value so ob-

TABLE I

	Nitrite crumb	P ₁	P ₂	P ₃	Rubbone-B	Rubbone-C
Molecular weight		24,200	11,800	4,000	3,600	2,400
Iodine value	<72,000	343	330	250	290	260
<i>Analysis</i>						
C	85.3	85.6	84.6	80.45	78.5	76.3
H	11.5	11.3	10.95	9.75	10.5	10.4
C/H ratio	7.41	7.58	7.72	8.25	7.48	7.34
N	0.6	0.2	0.03
Residue	0.6
O (by difference)	2.0	3.1	4.45	9.8	10.8	13.3
<i>Distribution of oxygen</i>						
% O with active H	0.52 (26%)	0.75 (24%)	1.6 (36%)	3.8 (39%)	*3.5 (31%)	4.1 (31%)
% O in -O-OH groups	0.008				0.001	0.06
% O in -CO ₂ H groups	0.09 (5%)		1.1 (25%)	2.4 (25%)	0.3 (3%)	0.3 (2%)
% O in -CO ₂ R groups	0.2 (10%)				1.5 (14%)	0.6 (5%)
% O in ≥C-OH groups	0.47 (24%)		1.1 (25%)	2.6 (27%)	*3.3 (29%)	4.0 (30%)
% O in >C : O groups	<0.02		1.4 (31%)	0.9 (9%)	0.7 (7%)	0.9 (7%)
Total oxygen accounted for	0.8 (40%)		3.6 (81%)	5.9 (60%)	5.8 (53%)	5.9 (44%)
Solubility in benzene	insol.†	sol.	sol.	sol.	sol.	sol.
Solubility in chloroform	insol.†	sol.	sol.	sol.	sol.	sol.
Solubility in carbon disulfide	insol.†	sol.	sol.	sol.	sol.	sol.
Solubility in acetone	insol.	sol.	sol.
Solubility in alcohol	insol.	insol.	insol.	sol.	insol.	sol.

* The sample of Rubbone-B used for this determination contained 11.3 per cent total oxygen.

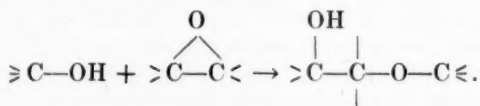
† The figures in brackets express the result as a percentage of the total oxygen.

† Nitrite crumb dissolved in these solvents on addition of 4.5 per cent piperidine.

tained, multiplied by 16, represents the sum of all the oxygen bound in alcohol groups plus half that present in the carboxyl and hydroperoxide groups ($\geq \text{C}\cdot\text{OH} + \frac{1}{2}-\text{CO}\cdot\text{OH} + \frac{1}{2}\geq \text{C}\cdot\text{O}\cdot\text{OH}$). For estimation of the carbonyl groups, the aluminium isopropylate procedure was used, the reagent yielding as the result of oxidation by the carbonyl groups an equivalent of acetone which was estimated in the form of its dinitrophenylhydrazone. It has been shown by Hilton⁷ that this method of determining acetone is accurate to within approximately 4 per cent when the quantities of reactants detailed below are used.

The results obtained are summarized in Table 1; for purposes of comparison, Hilton's results⁷ for Rubbone-B are included.

Discussion of results.—From the results in Table 1, it will be seen that little peroxide-oxygen remains in any of the rubbers, although it is regarded as the primary product of oxidation. This is not surprising as all the samples except nitrite crumb (which has by far the highest relative peroxidic-oxygen content) have been subjected to heat during their preparation, and the crumb had been stored for several years. However, if the peroxide groups are responsible for subsequent oxidation of the hydrocarbon, a large percentage of hydroxyl oxygen (from reduction of the hydroperoxide) would be expected, and this is, in fact, found in all the samples examined. At first it would appear that 50 per cent of the oxygen should be in hydroxylic form, but some of the hydroxyl groups react subsequently with carboxyl groups to give esters, and the remainder that is unaccounted for (17 per cent in the case of Rubbone-C) may have combined with epoxide groups to yield ethers.



Oxidative fission of the double bond of an isoprene unit should give rise initially to one carbonyl and one aldehyde group; the latter in so advanced an oxidized product is most probably oxidized to the carboxylic acid⁸, which may be subsequently converted to the ester. It follows, therefore, that each molecule of the oxidized product should contain at least one carbonyl and one carboxyl (or carbalkoxyl) group. Table 2, calculated from the previous re-

TABLE 2

Sample	Isoprene units per mol.	Functional groups per mol				
		-OOH	-CO ₂ H + -CO ₂ R	=COH	=CO	
Nitrite crumb	<1060	0.3	<15	<24	1	
P ₁	356	11*	...	
P ₂	173	...	8	8	10	
P ₃	59	...	6	7	2	
Rubbone-B	53	0.002	4	8	2	
Rubbone-C	36	0.09	1	6	1	

* Including carboxyl oxygen.

sults, shows that this is true. Although the figures are given only to the nearest whole number, in no case other than peroxide does this fall below unity.

The addition of acetic anhydride during the oxidation of the sample P₂ specifically affected the course of oxidation, giving rise to a greatly increased carbonyl content.

The results in Table 1 indicate that a considerable proportion of the oxygen in the rubbers remains unanalyzed. If it is assumed that reduction in unsaturation has been effected solely by addition of oxygen to the double bond (1 atom per double bond), the amount of oxygen required may be calculated. In the case of Rubbone-C, the iodine value has been reduced from 372 to 260, so that to a first approximation 30 per cent of the double bonds have been saturated. Thus each isoprene unit on the average will have increased in weight from 68 to 73, and to a second approximation the loss of unsaturation will be 32 per cent. The entry of oxygen which will correspond with this percentage is 7.5 per cent. If this value is added to the total oxygen accounted for by analysis (5.9 per cent), the sum obtained is 13.4 per cent, which is in good agreement with the 13.3 per cent obtained by difference from the carbon-hydrogen analyses. A similar calculation for Rubbone-B shows that the total oxygen should be 11.2 per cent, which is between the values of 10.8 and 11.3 per cent obtained from carbon-hydrogen analyses of different samples of this Rubbone. Such a calculation is not possible for the samples P₁, P₂ and P₃, as the case is complicated by the addition of phenol to the molecule. With nitrite crumb the calculated figure is too high (2.7 instead of 2.0), but this is probably explained by the fact that the iodine value used is a minimum figure (as the rubber did not dissolve) and may be considerably higher.

No satisfactory methods exist for the determination of epoxide and ethereal oxygen in rubbers, so that it is not possible to say whether most of the oxygen remains in the first form after addition to the double bond or whether it reacts in part with hydroxyl groups to form ethers. Reaction with diethylamine has been used as a method of epoxide determination⁹, but as the reagent also reacts with carboxyl, carbalkoxyl and conjugated carbonyl groups, the method is not capable of great accuracy. In addition it is by no means certain that all the epoxide groups in a rubber molecule are sufficiently reactive to be estimated in this manner.

It will be noticed from Table 1 that in nitrite crumb a large proportion (60 per cent) of the oxygen remains unanalyzed, some of which may have entered the rubber molecule in combination with nitrogen from the nitrous acid. In view of the extraordinary insolubility of the rubber, it seems probable that some type of cross-linkage between the chains has taken place; it is possible (although there is no definite evidence) that these links involve oxygen and nitrogen atoms. Such cross-linking may provide an explanation of the solubility of nitrite crumb in boiling xylene (the heat breaking the cross-links), as the rubber recovered from such a solution is obviously degraded, being more fluid in consistency and readily soluble in benzene. Nitrite crumb is also completely soluble in piperidine (or benzene containing at least 5 per cent piperidine), and this cannot be explained in terms of the alkalinity of the solvent as the rubber is only slightly acidic. On removing the solvent from such a solution the product is obviously of a much lower molecular weight, being a dark brown almost fluid material, like Rubbone. In effecting this breakdown the piperidine has itself entered the molecule in significant degree, as is evidenced by an increase in nitrogen content from 0.6 to 3.5 per cent. At present there is insufficient evidence to explain the mode of action of piperidine, an action not wholly shared by pyridine. Nitrite crumb does not dissolve in pyridine, but after long contact with the base, dissolution slowly occurs on addition of twice the volume of benzene.

EXPERIMENTAL

The microanalyses were carried out by W. T. Chambers and (Miss) H. Rhodes.

Solubility and preparation of samples of the oxidized rubbers for analysis.—*Rubbone-C.*—Rubbone (100 g.) was heated one hour under reflux with industrial methylated spirits (100 cc.). The mixture was allowed to cool to room temperature, the alcohol extract was decanted, and the alcohol-insoluble portion further extracted with methylated spirit (50 cc.). From the combined alcoholic extracts which contained Rubbone-C the solvent was removed on the water pump. As it is not possible to dry Rubbone samples to constant weight¹⁰ the material was dried in a high vacuum at room temperature for one week, and then stored in purified nitrogen at atmospheric pressure.

Nitrite crumb.—The rubber was dried in high vacuum to constant weight. Nitrite crumb was found to be quite insoluble in benzene, petrol, ether, chloroform, carbon disulfide and acetone, and soluble only in piperidine. This latter solution on evaporation *in vacuo* gave a brown viscous material, whose analysis is compared below with that of the original nitrite crumb. Extensive drying in a high vacuum failed to reduce the nitrogen content.

Nitrite crumb	C	H	N	Residue	O (difference)
Before dissolution	85.3	11.5	0.6	0.6	2.0
After dissolution	81.65	11.15	3.55	0.55	3.1

For the determination of molecular weight and of hydroperoxide, carboxyl, carbalkoxyl and carbonyl contents, a solution was prepared by heating 10 g. of nitrite crumb in 500 cc. of highly purified xylene at 120–140° C in a stream of nitrogen for two hours.

Rubber oxidized in phenol.—The author is indebted to D. A. Sutton for the following details respecting the preparation of the samples P₁, P₂ and P₃.

For P₁ pure phenol (100 g.) was heated to 170° C for 7 hours with 40 g. of acetone-extracted crepe in a stream of oxygen. The oxidation was stopped at this point, which marked the first appearance of only one phase in the reaction mixture.

For P₂ acetic anhydride was added with the idea of acetylating the hydroxyl groups as they were formed. Although this was not successful, the anhydride exercised a specific influence on the course of oxidation. The phenol (70 g.), acetic anhydride (10 cc.) and acetone-extracted crepe (20 g.) were heated together in a stream of oxygen for 10 hours at 170° C.

For P₃ phenol (70 g.) and acetone-extracted crepe (20 g.) were heated in oxygen as before for 23.5 hours.

The three samples were freed from phenol by distillation of the latter at 0.1 mm., followed by heating the residue at 60 to 100° C at the same pressure for 1 week.

Analyses.—After a week's drying the following results were obtained.

	C	H	N	Residue	O (diff.)	C/H ratio
Nitrite crumb	85.3	11.5	0.6	0.6	2.0	7.41
	85.05	11.55	...	0.7
P ₁	85.55	11.2	3.25	7.64
	85.6	11.4	3.0	7.51
P ₂	84.5	10.9	4.6	7.75
	84.7	11.0	4.3	7.70
P ₃	80.45	9.75	9.8	8.25
Rubbone-C	76.3	10.4	0.027	...	13.3	7.34
	76.25	10.4	0.029	...	13.3	7.34

Unsaturation.—Residual unsaturation was measured by determination of the iodine values of the oxidized rubbers¹¹, and the following results were obtained:

Nitrite crumb	340, 343	P ₁	243, 250, 263
P ₁	345, 342	Rubbone-C	258, 261
P ₂	329, 332		

Owing to the insolubility of nitrite crumb and the impossibility of using piperidine or xylene to promote dissolution before the iodine value determinations, it was necessary to carry out the estimation on solid nitrite crumb swollen in a mixture of chloroform (70 per cent), carbon disulfide (25 per cent) and acetic acid (5 per cent). The results for nitrite crumb, therefore, represent minimum figures.

Determination of peroxidic oxygen.—The peroxide contents of Rubbone-C and nitrite crumb were determined by the colorimetric method of Bolland *et al.* (*loc. cit.*) and the following results were obtained:

Nitrite crumb 0.008 per cent	Rubbone C 0.064 per cent
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As either method of dissolving nitrite crumb, *i.e.*, the use of piperidine or of heat, would destroy any peroxide present, this determination was carried out with solid crumb (0.1 g.) swollen with 2 cc. of peroxide-free benzene. The value obtained is therefore probably too low.

Determination of acidic oxygen.—To a 2 or 4 per cent solution of the oxidized rubber (1 g.) in xylene (50 cc.) or benzene (25 cc.) was added an equal volume of ethanol, and the mixture was titrated against 0.1 *N* aqueous sodium hydroxide. Employing either bromothymol blue or thymolphthalein as indicator, the titration was continued until the solution was just green. This color change was easier to observe than the yellow-red change with phenolphthalein. It was found with Rubbone-C that thymolphthalein (pH 9.3–10.5) gave a slightly higher acidic value than bromothymol blue (pH 6.0–7.6), indicating that some of the acidity was of a weak nature. All titrations were carried out in a stream of nitrogen.

	Bromothymol blue (percentage)	Thymolphthalein (percentage)
Nitrite crumb	...	0.09 0.10
P ₂	...	1.08 1.07
P ₃	...	2.39
Rubbone-C	0.17, 0.20, 0.22, 0.21	0.26 0.26

As in this determination nitrite crumb was precipitated on addition of alcohol, it was thought that it might be more accurate to add to the solution excess (50 cc.) of cold 0.05 *N* alcoholic potassium hydroxide and immediately to back-titrate with 0.1 *N* sulfuric acid (aqueous).

Nitrite crumb	0.07%, 0.10%
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Determination of hydroxylic oxygen (a) Rubbone-C and Samples P₁, P₂, P₃.—The Zerewitinoff method of active hydrogen determination as adapted for high vacuum technique by Bolland¹² was used with slight modification. The upper limb of the apparatus was made wider ($\frac{5}{8}$ inch tube with B19 cone), so that the oxidized rubber (20 mg.) could be introduced in a shallow tube. The rubber was dried *in vacuo* for 1–2 hours before the Grignard solution (a saturated solution to which an equal volume of xylene had been added) was

introduced into the other limb. Degassing of the reagent was carried out as usual, and 1-2 cc. of xylene was distilled over on to the oxidized rubber, which dissolved in 1-2 hours. The solutions were mixed and the evolved methane measured on a McLeod gauge in the customary manner.

Found: P₁, 0.75 per cent oxygen associated with active hydrogen; P₂, 1.64 and 1.58 per cent; P₃, 3.78 per cent; Rubbone-C, 4.13 and 4.10 per cent.

(b) *Nitrite crumb*.—*Method I*.—Into one limb of the usual apparatus was introduced a weighed amount (0.05 g.) of crumb, which was then dried *in vacuo*. Sodium-dry xylene (2 cc.) was added and frozen in liquid air, while all air was removed from the apparatus. Dry nitrogen (passed over calcium chloride and through a liquid air trap) was introduced until the pressure was about half atmospheric. The rubber was heated with the solvent at 120° C for about 2 hours, and then shaken gently. The determination was continued as above.

Method II.—The only difference in this method was that the solvent was distilled from the Grignard solution contained in the other limb of the apparatus. This ensured freedom from adventitious active hydrogen.

	I	II
Nitrite crumb	0.64%	0.52%, 0.52% oxygen associated with active hydrogen.

The complete agreement in method II must be regarded as accidental; the possible error is of the order of ± 0.05 per cent.

Determination of carbalkoxylic oxygen.—A 2 per cent solution of nitrite crumb (1 g.) in xylene, or a 4 per cent solution of Rubbone-C (1 g.) in benzene was refluxed with 2.5 cc. 0.1 N alcoholic potassium hydroxide for 4 hours in a slow stream of nitrogen. After cooling, ethanol was added (where necessary) to increase the alcohol to hydrocarbon ratio to 1:1, and the solution was diluted with water to 200 cc. The excess alkali was titrated against 0.1 N sulfuric acid, using bromothymol blue as indicator, and a blank determination using only the reagents was carried out. It was found that longer refluxing with alkali did not affect the result.

	Oxygen in CO ₂ H + CO ₂ R	CO ₂ R (by difference)
Nitrite crumb	0.36%, 0.32%, 0.27%	0.2%
Rubbone-C	0.83%, 0.84%	0.58%

Determination of carbonyl oxygen.—A 4 per cent toluene solution of the oxidized rubber (1 g.) (except for nitrite crumb, where a 2 per cent xylene solution was used) was heated with aluminum isopropylate and isopropyl alcohol as in the method described by Hilton⁷, and the acetone formed was estimated as its 2,4-dinitrophenylhydrazone.

In the case of sample P₁ and of nitrite crumb no precipitate of the dinitrophenylhydrazone formed so that the amount of oxygen contained in carbonyl groups must certainly be less than 0.02 per cent.

Nitrite crumb	None found
P ₁	None found
P ₂	1.40%
P ₃	0.87%
Rubbone-C	0.83%, 0.91%, 0.85%

Blank determinations were carried out, omitting in two successive experiments the isopropylate and the Rubbone-C, but in neither case was any acetone dinitrophenylhydrazone precipitated.

ACKNOWLEDGMENT

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STRUCTURAL FEATURES OF BUNA-S. RELATION TO PHYSICAL PROPERTIES *

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The low tensile strength of Buna-S gum stocks is generally believed to be due to failure to obtain effective cross-linkage as the result of vulcanization with sulfur and accelerators. Combined with this is the complete absence of crystallization of Buna-S on stretching which, in the case of natural rubber, reinforces and strengthens the vulcanized gel structure.

The absence of crystallization in Buna-S can be explained on the basis of nonsymmetry along the polymer chains. Strictly speaking, Buna-S is not a true polymer, for ozonolysis shows that the styrene units are not spaced evenly in the chain but are grouped together in some locations¹. Ozonolysis also has proved the presence of vinyl groups attached to the chain, resulting from the polymerization of butadiene in the 1,2 instead of the 1,4 position¹. These vinyl groups must be unevenly spaced along the chain, and mixed *trans* and *cis* isomers must be present.

Figure 1 illustrates the chemical units present in Buna-S, rubber, and gutta-percha hydrocarbons. In a Buna-S copolymer containing 24.5 per cent of styrene, there are six butadiene to one styrene units. It appears¹ that about one butadiene in five polymerizes in the 1,2 position in the chain. It should be emphasized that, in Buna-S, ozonolysis¹ has shown that no regular order exists in the location of A, B, and C units in the polymer. An entire lack of symmetry in the positioning of these units in the chain would be expected in view of the nature of the polymerization reaction.

Consequently, we can readily see how impossible it is for Buna-S to crystallize. Since double bonds in the butadiene chain units and in the vinyl groups are unevenly spaced along the chain, they cannot be uniformly or frequently matched up with those in neighboring chains. This fact may result in an ineffectual cross-linking of Buna-S chains with active sulfur atoms during vulcanization. In contrast, the more or less perfect chain symmetry of sol rubber hydrocarbon should result in a higher frequency of alignment of the double bonds and, therefore, a more effective vulcanization reaction to produce more frequent and more evenly spaced cross-links in the vulcanizates.

Where vinyl and benzene side groups are located in the Buna-S chain, the separation of adjacent chains will be considerably greater than in natural rubber chains with shorter methyl side-groups. This wider chain separation of Buna-S chains may also reduce effective cross-linking with sulfur during vulcanization and thereby cause weak areas in the vulcanizate structure.

Good physical characteristics of Buna-S vulcanizates can be obtained only by pigment reinforcement. The factors determining the extent and nature of this reinforcement are amount of loading, size and size distribution of pigment,

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shape of pigment particles, and dispersion quality or uniformity of separation of pigment particles in the vulcanizate. Because Buna-S does not wet pigments so readily as rubber, it is more difficult to obtain a uniform Buna-S stock in conventional rubber mixing equipment.

The physical properties of Buna-S compounds deteriorate faster with a rise of temperature than do those of natural rubber compounds. This behavior can be explained on the basis that the physical properties of Buna-S stocks depend to a greater extent on association forces and less on chemical cross-linking than do those of similar natural rubber vulcanizates. These association forces between the polymer chains and between the pigment particles and Buna-S chains are greatly reduced at elevated temperatures; a

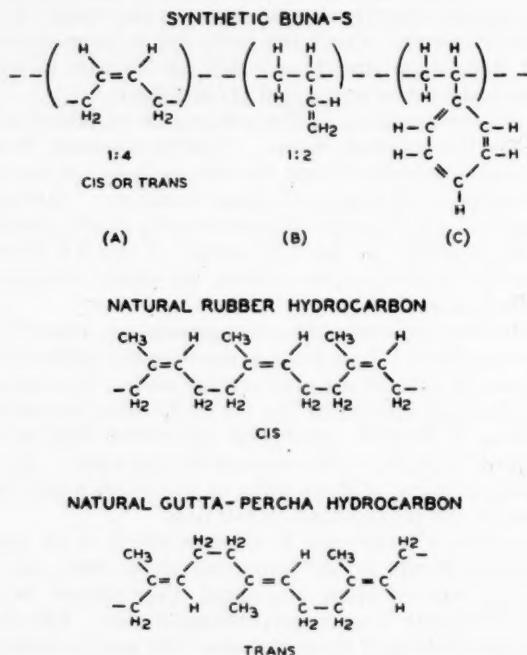


Fig. 1.—Chemical units in Buna-S, rubber, and gutta-percha hydrocarbons.

weaker gel structure results in Buna-S than in the more highly and effectively cross-linked rubber gel.

Gelation resulting from branch chaining and cross-linking may be present in Buna-S in widely varying degrees, depending on the polymerizing conditions and subsequent treatment of the polymer. In cases where the polymer is completely soluble in benzene, it will become increasingly insoluble in benzene or chloroform if antioxidant is absent and the polymer is exposed to air. For example, a pure white Buna-S polymer changed from 100 to 39 per cent benzene solubility on exposure to air at room temperature for 4 days, whereas no gain in weight could be detected on an ordinary analytical balance.

The rate of oxidation of purified Buna-S polymer is indicated by the weight gain curves for two different preparations in finely cut form in Figure 2. After

64-days' exposure to air in the laboratory, the material became yellowish, and was hard and brittle on the outside surfaces. Gelation also takes place in solution in the absence of antioxidants. Pure rubber hydrocarbon absorbs oxygen somewhat more rapidly than Buna-S hydrocarbon when exposed to air but, unlike the Buna-S hydrocarbon, it remains soluble in chloroform². Possibly the vinyl side-groups in Buna-S may be the seat of oxygen cross-linking, which results in gelation. It is well known that a complete gelation of linear polymers can result from a limited number of cross-links.

Improvements in Buna-S from a structural point of view are made extremely difficult if not impossible by the fundamental nature of the polymerization reaction, which leads to the features of chain asymmetry just described. Aside from a small amount of gel, not only does the rubber hydrocarbon in crude rubber possess chain symmetry, but it is all in the *cis* configuration.

Another weakness of Buna-S is poor processing characteristics. It is very nervy, and its compounded stocks show a large shrinkage when slabbed off a mill following mixing and cooling. A shrinkage of 40 per cent in length is

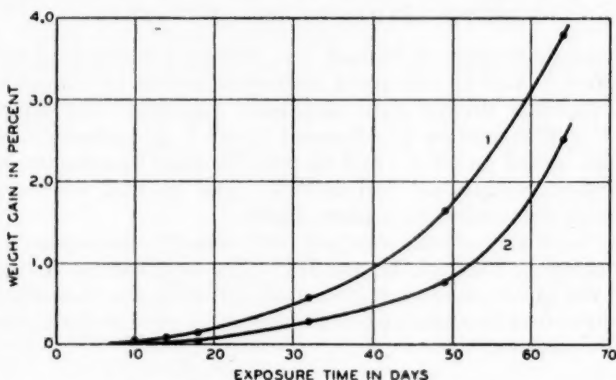


FIG. 2.—Rate of oxidation of Buna-S hydrocarbon.

not uncommon. A lack of tackiness or cohesive bonding to itself is also a well known defect of Buna-S. The nerve or poor processing is due to the presence of a high-molecular-weight fraction associated with a considerable portion of soft, liquid, low polymers. In other words, Buna-S has too broad a distribution of polymer sizes. These large molecules are highly elastic and, if deformed, spring back when the distortion force is removed.

The presence of the liquid low polymers together with the excessive amount of stearic acid and other nonhydrocarbon components is also objectionable; they contribute to poor wetting of pigments and poor vulcanization which, in turn, lead to deficient physical properties.

When crude rubber is broken down by mastication, the large molecules are placed under strain and, in the presence of ozone and oxygen, are split into shorter segments. A well masticated crude rubber is made up of polymer units with a narrow range in chain length³ since the longer chains are apparently preferentially split.

A considerable improvement in the processing characteristics of Buna-S would result if a narrower range of polymer sizes could be effected. This new range should contain a lower-molecular-weight high fraction and should elimi-

nate the lowest-molecular-weight fractions, which vary from oils to a taffylike substance. In any case, gelation of the polymer should be prevented. As long as the present higher-polymer fractions remain, the removal of the lower fractions results in a dry, nery polymer which is practically unmanageable on the mill.

This paper presents data on the fractionation of a benzene-soluble type of Buna-S polymer. Data are given on the effect of fractionation of Buna-S on the nature of vulcanizates made from different fractions. The effect of polymer size on the chloroform extract obtained after acetone extraction of the vulcanizates is also reported. This chloroform extract is a soft pasty solid, having a composition like the vulcanized hydrocarbon. It has a very low molecular weight, and tends to crystallize in long fernlike needles. Its presence appears to result from the smaller polymer molecules which react with sulfur intramolecularly but not intermolecularly, and therefore remain soluble in chloroform. A small amount of chloroform-extractable crystalline substance is present in vulcanized crepe rubber.

FRACTIONATION BY PRECIPITATION

A benzene-soluble type of Buna-S was dissolved in benzene to form a 2 per cent solution. A 50-50 mixture of methanol-benzene by volume was added slowly with vigorous stirring until cloudiness appeared. All solutions were kept at 20° C. The solution was warmed to 40° C to redissolve the precipitated polymer, cooled to 20° C, and allowed to stand overnight; during this time the fraction precipitated and settled. The fraction was separated by decantation and coagulation with pure alcohol.

Data on the fractionation, analysis, and relative chain-lengths of these fractions are given in Tables I, II, and III. The first fraction is large in comparison with the others, because only a small spread in the quantity of alcohol used for precipitation was required to throw a large part of the high-molecular fraction out of solution.

TABLE I
FRACTIONATION OF BUNA-S

Hydrocarbon fraction	Methanol added (percentage by volume)	Percentage yield		Description
		On Buna-S	On total hydrocarbon	
1	19.5	37.0	40.0	Moderately tough and elastic, not tacky
2	20.3	10.0	10.9	Somewhat elastic, not tacky
3	21.2	9.3	10.1	Soft, plastic, stringy, not tacky
4	22.3	8.7	9.5	Soft, taffylike, somewhat tacky
5	24.5	8.0	8.6	Soft, taffylike, very plastic and tacky
6	28.5	8.0	8.6	Highly viscous, sticky liquid
7	38.0	6.3	6.8	Viscous, sticky liquid
8 ^a	...	5.0	5.5	Viscous oil
1A ^b	19.3	23.0	24.9	Tough and elastic, like smoked sheets

^a Supernatant liquid from Fraction 7 was evaporated to dryness, and residue repeatedly washed with hot methanol, followed by one cold acetone wash to remove nonhydrocarbon substances; residue was Fraction 8.

^b Fraction 1 was redissolved in benzene, containing antioxidant, to form a 0.5% solution. A 50-50 methanol-benzene solution was added gradually with vigorous mechanical stirring to precipitate partially the higher-molecular-weight portion.

TABLE II
CHEMICAL ANALYSIS OF BUNA-S FRACTIONS

Fraction no.	Carbon (%)	Hydrogen (%)	C/H ratio	Ash (%)	Iodine no.	Styrene percentage from	
						C/H	I no. ^a
1	88.90	10.37	8.57	0.88	356.1	21.3	23.4
2	88.97	10.32	8.61	0.19	359.3	22.5	22.7
3	88.97	10.27	8.66	0.27	359.1	24.1	22.8
4	89.26	10.26	8.70	0.18	359.8	25.4	22.6
5	89.27	10.29	8.64	0.29	359.6	23.5	22.7
6	88.57	10.33	8.58	0.89	355.5	21.6	23.5
7	88.06	10.30	8.56	0.98	352.1	21.0	24.3
8	87.74	10.25	8.55	0.35	348.1	20.7	25.2
Whole hydrocarbon ^b	88.27	10.25	8.63	0.80	356.7	23.2	23.3

^a Styrene content = $\frac{(465 - \text{iodine No.}) \times 100}{465}$

^b Acetone-extracted GR-S

TABLE III
POLYMER LENGTH OF BUNA-S FRACTIONS IN COMPARISON WITH NATURAL RUBBER^a

Polymer fraction	C	Φ	η	(η)	$\frac{\log \eta}{\Phi}$	N*	N ₁
1	0.218	0.00234	2.32	3.84	156.2	3577	2693
2	0.300	0.00322	1.98	2.28	92.1	2109	1589
3	0.432	0.00465	2.08	1.69	68.4	1566	1180
4	0.400	0.00430	1.66	1.26	51.2	1172	883
5	0.609	0.00655	1.69	0.86	34.8	797	600
6	0.446	0.00469	1.27	0.54	22.1	506	381
7	0.642	0.00690	1.21	0.30	12.0	275	207
8	2.610	0.02801	1.66	0.19	8.0	183	138
1-A	0.101	0.00109	1.85	6.09	245.1	5613	4228
Whole	0.185	0.00197	1.60	2.54	103.6	2372	1787
Buna-S							
Hydrocarbon							
Unmilled	0.304	0.00327	1.97	2.23	90.0	...	1542
5 min. on cool roll	0.348	0.00374	1.97	1.95	78.7	...	1358
10 min. on cool roll	0.349	0.00375	1.96	1.93	77.7	...	1340
30 min. on cool roll	0.342	0.00368	1.88	1.84	74.5	...	1285
60 min. on cool roll	0.350	0.00376	1.82	1.70	69.2	...	1194
Crepe							
Whole sol	0.049	0.000527	1.41	6.99	283.1	6285	...
Milled 15 min., 96° C ^b	0.221	0.00238	1.70	2.40	96.9	2152	...
Milled 15 min., 35° C ^b	0.476	0.00512	1.81	1.24	50.3	1117	...
Milled 200 min., 35° C ^b	0.313	0.00337	1.32	0.83	35.8	795	...

^a Nomenclature:

C = grams per 100 cc. of solution

N = average number of carbon atoms in chains

Φ = cc. of solute per cc. of solution

$N = \frac{\log \eta W}{\Phi K_{co}}$; $N_1 = \frac{\log \eta W_1}{\Phi K_{co}}$

W = 0.734 based on 23.4% styrene in Buna-S used

W = 0.71 in case of natural rubber

W₁ = 0.552, assuming 30% 1,2 addition of butadiene in Buna-S

K_{co} = 0.032

* See Kemp and Peters⁴

^b Mill roll temperature

Figure 3 shows the effect of alcohol on the precipitation of Buna-S hydrocarbon from benzene solution. Each point on the curve represents a fraction of precipitated hydrocarbon which was removed by decantation of the supernatant liquid followed by the addition of more pure alcohol to harden the coagulum so it could be removed. The fractions were dried under vacuum at 50° C in a stream of lamp nitrogen and weighed.

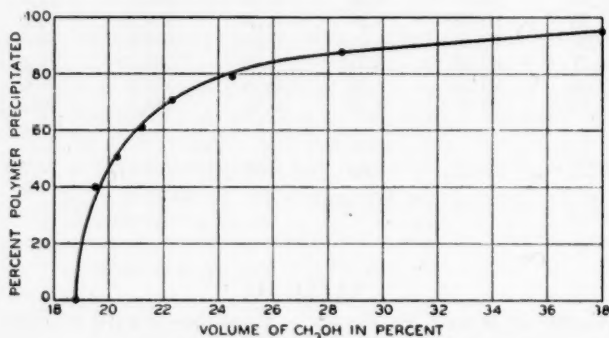


FIG. 3.—Relation of alcohol content to precipitation of Buna-S from benzene solution.

In Figure 4 average chain length is plotted against percentage of each fraction. It must be realized that each fraction still contains polymer units of varying sizes, as one fractionation is only partially effective in separating the different sized specimens present. In no case can one expect to approach perfection in any number of repeated fractionations.

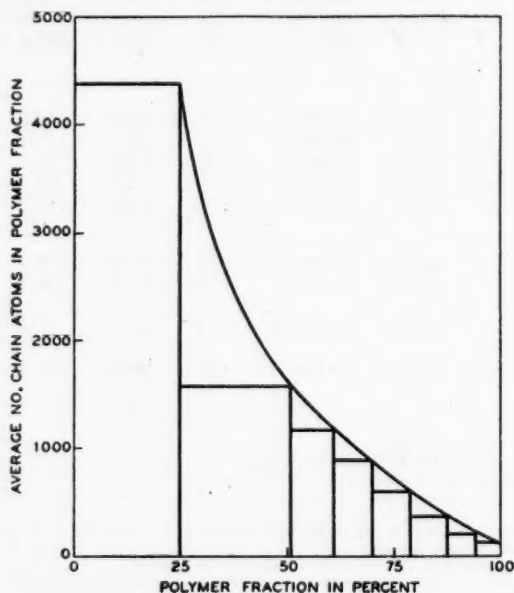


FIG. 4.—Molecular weight distribution of Buna-S.

If Buna-S with narrow polymer distribution could be prepared with average chain lengths in the range of Fractions 2 or 3 (Table III), a much needed improvement in processing would result. Better control of the polymerization reaction is needed to accomplish this. The physical properties of pigment-loaded stocks probably would not be greatly improved by such a change for reasons already stated although hysteresis and heat build-up might be improved.

The expression of polymer size by chain atom lengths (Table III) is desirable; it places polymers of questionable chain linearity on a more comparable basis with those whose chains are more certain to be linear. Since average polymer length determines viscosity, the argument for using this term in comparing polymers is apparent.

EFFECT OF REMOVING LOW POLYMERS

Two hundred grams of Buna-S were sheeted out to a thickness of about 0.002 inch on a laboratory mill, cut into 1-inch strips, and dropped separately into a 5-liter round-bottom flask containing 4 liters of a 20.2 per cent by volume mixture of methanol in benzene. The flask and its contents were placed in the dark, and kept at room temperature (18–23° C). On standing, the Buna-S slowly changed into a liquid, swollen gel which collected on the bottom of the flask. After one week the extract was decanted, and 4 liters of fresh solvent were added. This time the concentration of methanol in benzene was reduced to 19.2 per cent to hasten the extraction process. From time to time during the next two weeks the mixture was thoroughly agitated, and at the end of this time the extract was replaced with fresh solvent. The concentration of methanol in benzene was then 20 per cent by volume. During the following week the mixture was agitated as before. Finally, the extract was decanted, 1.5 per cent of Neozone-D was added to the gelatinous mass, and it was coagulated with pure methanol. The coagulum was pressed and placed in a vacuum oven at 40° C until free of solvent. Its weight was 116 grams, or 58 per cent of the original material.

Aliquots from the various extracts were dried in a weighed crystallizing dish, weighed, and then dissolved in 100 cc. of pure benzene. The viscosity of the benzene solutions was determined in an Ostwald viscometer at 25° C. The results are given in Table IV.

TABLE IV
VISCOSITY OF BENZENE SOLUTIONS OF EXTRACTS 1, 2, AND 3

Extract no.	Concentrated methanol in benzene (percentage)	Extraction (weeks)	Percentage extracted	Log η_r/c
1	20.2	1	8.0	...
2	19.2	2	16.0	0.342
3	20.0	1	16.5	0.372

The extracted Buna-S was very tough, had little plasticity, and sheeted out on the laboratory mill rolls with difficulty. It resembled closely the higher-molecular-weight fractions of Buna-S rubber which had been separated by fractional precipitation. It was soluble to the extent of 99 per cent in benzene, and the log η_r/C value for this solution was 1.13. The average log η_r/C value for the highest-molecular-weight fractions of Buna-S, which represent 60 per cent by weight of the polymer, was found to be 1.34. The

lower $\log \eta_r/C$ value of the former probably resulted from breakdown during the sheeting-out operation. It is also probable that more of the low-molecular-weight copolymer molecules remained in the extracted material than in the case where precipitation procedure was employed.

Table V gives the composition of compounds prepared with extracted

TABLE V
TENSILE STRENGTH DATA ON OPTIMUM CURES

Compound no.		1	2	3	4	5
Regular Buna-S		100.00	100.00			
High-mol.-wt. Buna-S		100.00	100.00	...
Smoked sheet		100.00
Statex black		...	50.00	...	50.00	...
Zinc oxide XX-72		10.00	10.00	10.00	10.00	10.00
Stearic acid		2.00	2.00	5.00	5.00	5.00
Sulfur		0.50	2.00	0.50	2.00	0.30
Accelerator 808		0.75	0.75	0.75	0.75	0.75
Tetramethylthiuram monosulfide		0.10	0.10	0.10	0.10	0.10

Compound no.	Cure (min. ° F)	Rate of extension (in. per min.)	Lbs. per sq. in.		Elongation at break (percentage)	(Hardness Shore A)
			Modulus at 300%	Tensile strength		
1	45 (280)	22	50	875	1125	25
2	60 (280)	22	1350	3150	575	57
3	45 (280)	22	250	670	520	37
		22	180	750	610	
		22	260	920	650	
		12	290	750	610	
		12	210	820	650	
4	60 (280)	22	2400	3380	350	65
		22	2370	3070	320	
		22	2360	3380	370	
		12	2470	3350	370	
		12	2340	3040	350	
5	40 (280)	22	50	26
		22	50	1400	900	
		22	50	1300	900	
		12	50	1720	950	
		12	50	1460	970	

Buna-S, two similar compounds made with the original Buna-S, and one made with natural rubber. The two regular Buna-S compounds (1 and 2) were mixed according to the War Production Board mixing schedule. The two high-molecular-weight Buna-S compounds (3 and 4) and natural rubber compound 5 were mixed on the regular 12-inch laboratory mill with special guides to reduce the working length of the mill rolls to 5 inches.

The mixed compounds were permitted to stand overnight, refined twice through tight mill rolls, and vulcanized in a 0.075-inch-thick mould. There was just enough compound to make one 6 × 6 inch sheet cure. After vulcanization the cured sheets were placed in the aeration rack in a constant temperature-humidity room for 24 hours. They were then removed, and five tensile test-specimens were cut from each sheet with a razor-sharp 1/4-inch dumbbell die. The results of tensile strength tests on optimum cures are

shown in Table V. The rate of extension of the specimens was changed from 22 to 12 inches per minute. The results show that this had no effect on tensile strength values.

ACETONE AND CHLOROFORM EXTRACTION

One-gram samples of the optimum cured compounds (1 to 5) were diced and extracted with acetone in the regular extraction apparatus for 20 hours. They were then chloroform-extracted for a total time of 48 hours, the chloroform being replaced at the end of 24 hours. Results and physical properties are given in Table VI. During the chloroform extractions compounds 2 and 4

TABLE VI

DATA ON ACETONE AND CHLOROFORM EXTRACTIONS OF COMPOUNDS 1 TO 5

Compound no.	Acetone extract (percentage)	Chloroform extract (percentage)		Total (percentage)
		0-24 hrs.	24-48 hrs.	
1 (regular Buna-S gum)	10.33	Continuously		15.4
2 (regular Buna-S-Statex)	7.35	3.13	0.81	3.94
3 (high-mol.-wt. fraction Buna-S gum)	7.01	4.44	1.67	6.11
4 (high-mol.-wt. fraction Buna-S-Statex)	4.21	0.82	0.83	1.65
5 (natural rubber gum)	6.04	5.54	1.14	6.68

Compound no.	Acetone extract	Chloroform extract	
		0-24 hrs.	24-48 hrs.
1	Brown and oily	Colorless, viscous, tacky	
2	Brown, viscous, partly crystalline	Colorless, tacky, vis- cous	Colorless, glassy
3	Brown, viscous, partly crystalline	Colorless, tacky, vis- cous	Colorless, glassy
4	Brown, viscous, partly crystalline	Colorless, viscous	Colorless, glassy
5	Yellowish, partly crystalline	Colorless, partly crystalline	Colorless, glassy

(Statex black) swelled very little; compounds 1 and 3 (pure gum) swelled considerably and to about the same extent. Compound 5 (natural rubber) swelled to about the same extent as did the Buna-S gum compounds.

The acetone and chloroform extracts of both pure-gum and Statex black high-molecular-weight Buna-S compounds were reduced considerably. It is of interest to note the lower chloroform extract of those stocks containing Statex black. It appears possible that carbon black tends to bond the smaller Buna-S molecules. The physical properties of the extracts are also described. Kemp and Peters⁶ showed that crepe rubber contains a small percentage of low-molecular polymer which, combined with the low sulfur content in compound 5, probably accounts for its substantial chloroform extract.

EFFECT OF DIFFERENT ACCELERATORS

The three compounds in Table VII were prepared to test the effect of acid and alkaline type accelerators on the vulcanization of Buna-S. The mixing schedule was slightly modified in that Buna-S was allowed to work only 1.5 minutes before the compounding ingredients were added, compared with 10 minutes recommended by the WPB schedule. Table VII gives the physical

TABLE VII
EFFECT OF ACCELERATORS ON PHYSICAL PROPERTIES

Compound no.	6		7		8	
Buna-S	100.0		100.0		100.0	
Bardol	5.0		5.0		5.0	
Zinc oxide XX Red 4	5.0		5.0		5.0	
Sulfur	2.0		2.0		2.0	
Mercaptobenzothiazole	1.5		
Diphenylguanidine	...		1.5		...	
Accelerator 808		1.5	
	113.5		113.5		113.5	

Cure (min. at 292° F)	Original tests			Air-aged 7 days at 100° C		
	Lbs. per sq. in. Modulus at 300%	Tensile strength	Elongation at break (percentage)	Lbs. per sq. in. Modulus at 300%	Tensile strength	Elongation at break (percentage)
Compound 6 (Captax)						
20	25	220	920
30	50	180	650
40	70	150	510
50	70	180	510
60	70	180	420
120	120	157	377
Compound 7 (DPG)						
20	None	None	250	40	130	620
30	None	None	2200	60	210	610
40	None	230	1500	100	250	550
50	17	290	1330	100	290	530
60	23	160	907	140	180	360
120	50	220	640	220	220	295
Compound 8 (808)						
20	95	575	715	230	340	370
30	90	590	650	210	340	360
40	115	520	620	225	285	360
50	120	450	575	200	380	420
60	110	510	610	220	400	420
120	150	420	500	220	290	350

TABLE VIII
DATA ON ACETONE AND CHLOROFORM EXTRACTION OF COMPOUNDS 6, 7, AND 8

Compound no.	Cure (min. at 292° F)	Acetone extract (percentage)		Chloroform extract (percentage)	
		Unaged	Aged	Unaged	Aged
6 (Mercaptobenzo- thiazole)	20	14.89	...	13.90	...
	50	12.77	...	6.04	...
	120	11.98	...	4.34	...
7 (Diphenylguani- dine)	20	14.03	9.03	25.81	10.65
	50	13.80	7.50	19.47	4.55
	120	11.41	6.43	7.29	1.85
8 (808)	20	11.03	7.35	7.91	2.39
	50	10.78	7.00	5.94	2.54
	120	10.37	6.66	4.84	2.41

properties of the cured sheets after conditioning at 75° F and 45 per cent relative humidity and of the same cures after aging for 7 days in the hot air

TABLE IX
CHEMICAL ANALYSIS OF CHLOROFORM EXTRACT OF DPG STOCK 7,
CURED 50 MINUTES AT 292° F

Hours' extraction	C (%)	H (%)	S (%)	Ash (%)	Iodine no.	C/H ratio	Styrene from I/no.	Extract (percentage)
18	87.57	10.31	1.26	0.10	350.3	8.49	22.2	11.8
18-45	87.45	9.87	1.31	0.27	344.7	8.84	23.3	4.14

oven at 100° C (212° F). The acetone and chloroform extraction data on these compounds are given in Tables VIII and IX.

Compound 7 swelled most when chloroform-extracted, compound 6 was intermediate; compound 8 swelled least. The 7-day-aged samples swelled only about half as much as did the unaged samples. The acetone extract of each unaged compound was brown and viscous; the chloroform extracts were

TABLE X
VISCOSITY OF BENZENE SOLUTIONS OF EXTRACTS 6, 7, AND 8

Extract	Cure (min.)	Concentration (g. per 100 cc.)	η	$\frac{\log \eta}{c}$
6 (Mercaptobenzothiazole)	20	1.254	1.51	0.143
7 (Diphenylguanidine)	50	2.012	2.19	0.169
8 (808)	20	0.769	1.15	0.079

colorless viscous liquids which, on standing, crystallized into radial monoclinic crystals arranged into a fern-shaped pattern.

The relative viscosities and $\log \eta/C$ values of benzene solutions of the chloroform extracts of each of the three compounds are given in Table X.

The 808-accelerated Buna-S compound 8 possessed the best physical properties of the three studied. Its acetone extract was lower than that of the other two stocks. With an increase in time of cure, the chloroform extracts

TABLE XI
FORMULAS OF TREAD COMPOUNDS 9, 10, 11, AND OF PURE GUM COMPOUNDS 12, 13, 14

Compound no.	9	10	11
Buna-S	100	100 ^a	100 ^b
Bardol	5	5	5
Zinc oxide XX-4	5	5	5
Kosmobile-77	50	50	50
Sulfur	2	2	2
Mercaptobenzothiazole	1.5	1.5	1.5
Stearic acid	...	4.0	4.0
Cure	50 minutes at 292° F		
Compound no.	12	13	14
Buna-S	100	100 ^a	100 ^b
Zinc oxide XX-72	10	10	10
Stearic acid	2	6	6
Sulfur	0.75	0.75	0.75
808	0.75	0.75	0.75
Tetramethylthiuram monosulfide	0.10	0.10	0.10
Cure	20 minutes at 260° F		

^a High molecular weight

^b Low molecular weight

TABLE XII
PHYSICAL PROPERTIES OF TREAD COMPOUNDS 9, 10, AND 11

Compound no.	Modulus (lbs. per sq. in.)					Tensile strength (lbs. per sq. in.)	Elongation (%)	Hardness (Shore A)	Acetone extract (percentage)	Chloroform extract (percentage)
	100%	200%	300%	400%	500%	600%	700%			
9	...	478	990	1500	2050	2515
10	240	715	1500	2475	3585	57	5.70	1.58
11	110	270	550	815	1125	1440	1730	47	6.56	8.73

* Dry extract partly crystalline

TABLE XIII
PHYSICAL PROPERTIES OF PURE GUM COMPOUNDS 12, 13, AND 14

Compound no.	Modulus (lbs. per sq. in.)										Tensile strength (lbs. per sq. in.)	Elongation (%)	Hardness (Shore A)	Acetone extract (percentage)	Chloroform extract (percentage)
	100%	200%	300%	400%	500%	600%	700%	800%	900%	1000%					
12	40	65	100	170	250	400	620	1000	1170	1025	...	10.23	10.16
13	60	220	465	750	825	425	40	5.23	2.45
14	25	60	105	165	265	365	1075	17	8.14	16.89

* Dry extract partly crystalline

decreased. After air-oven aging at 100° C for 7 days, all the stocks had lower acetone and chloroform extracts. The tensile strength at optimum cure of the diphenylguanidine stock remained unchanged. Under the same conditions compound 8 decreased in tensile strength and elongation at break but showed a substantial increase in modulus.

When the chloroform extracts of the three stocks were dissolved in benzene and their relative viscosities determined, the chloroform extract of the diphen-

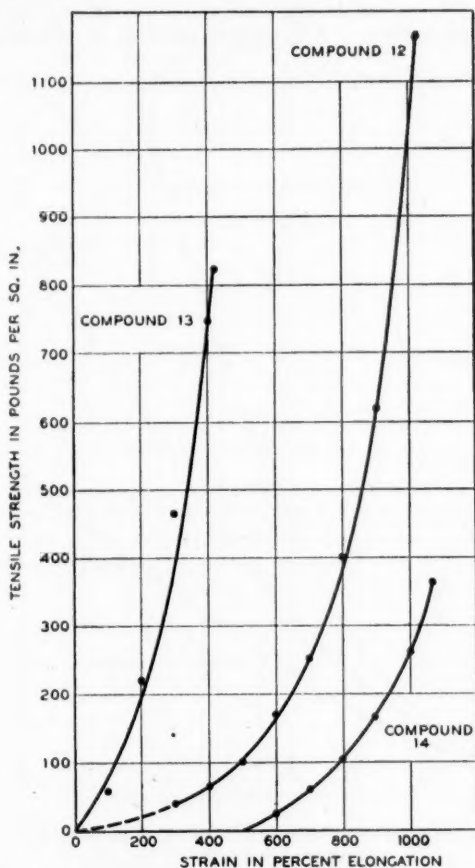


Fig. 5.—Stress-strain curves of regular and fractionated Buna-S pure-gum compounds, cured 20 minutes at 260° F.

ylguanidine-accelerated stock had the highest $\log \eta_r/C$ value and the 808-accelerated stock had the lowest. The degree of swelling of the compounds in hot chloroform was inversely proportional to the time of cure and aging of Buna-S.

HIGH- AND LOW-MOLECULAR WEIGHT FRACTIONS

As a further check on the effect of molecular weight on the vulcanization of Buna-S, 124 grams of the high-molecular-weight portion of Buna-S were pre-

pared as follows, using benzene-soluble Buna-S from the same lot employed in the previous fractionation: Five 50-gram portions of Buna-S were dissolved in 2500 cc. of c.p. thiophene-free benzene in separate 4-liter Erlenmeyer flasks. The solution was heated to 40° C, and 1525 cc. of a 50-50 benzene-methanol solution were slowly added with vigorous stirring. This resulted in a methanol concentration of 18.95 per cent, which was sufficient to precipitate the high-molecular-weight fraction of Buna-S. The flasks were set aside to cool slowly to room temperature, which resulted in precipitation. The flasks were placed in water at 20° C for several hours, and the supernatant liquid was then decanted from the precipitate. A 0.4-gram portion of Neozone-D was added

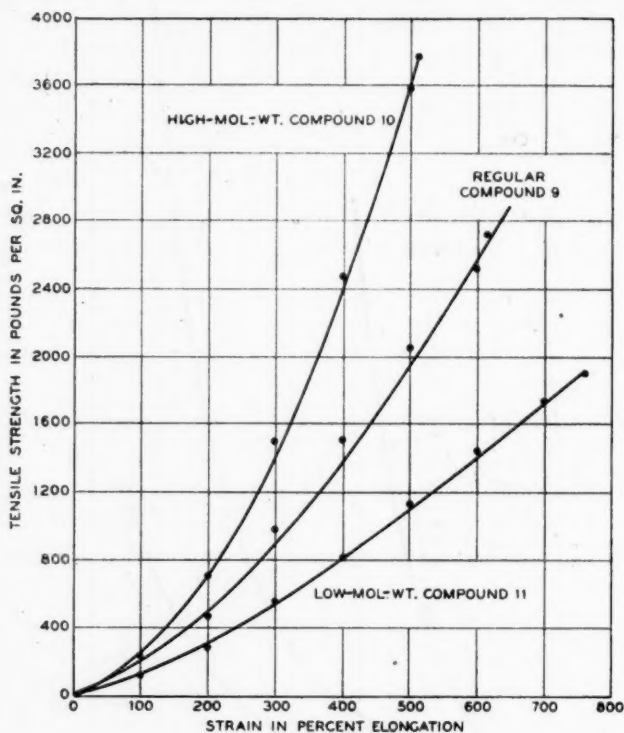


Fig. 6.—Stress-strain curves of regular and fractionated Buna-S tread compounds, cured 50 minutes at 292° F.

to the gelatinous precipitate in each flask, and the coagulum was solidified by adding more 50-50 benzene-alcohol and finally pure alcohol. The high-polymer fraction was dried under an 8-cm. vacuum in a stream of lamp nitrogen. The yield was 45.6 per cent of the original Buna-S. To the decantate was added pure methanol to a 40.13 per cent alcohol concentration. After the temperature was brought to 20° C as before, the supernatant liquid was decanted from the coagulum. The coagulum was dried as before, and the yield was 40.1 per cent of a soft, tacky, plastic product. The $\log \eta_r/C$ value of the high fraction was 1.86, of the low fraction 0.50, and of the whole Buna-S 0.97.

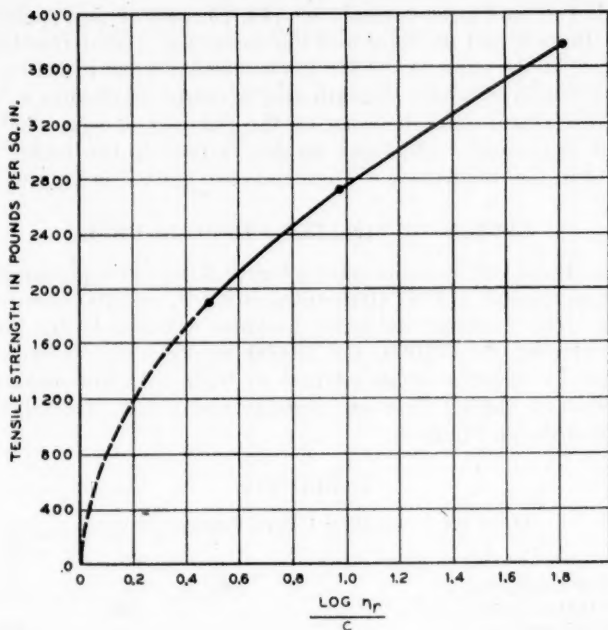


Fig. 7.—Tensile strength of tread compounds vs. molecular weight index of starting Buna-S.

Compounding was carried out under carefully standardized conditions on a small Thropp mill. The compositions of the tread stocks (9, 10, and 11) are given in Table XI; results of physical tests are listed in Table XII. Addi-

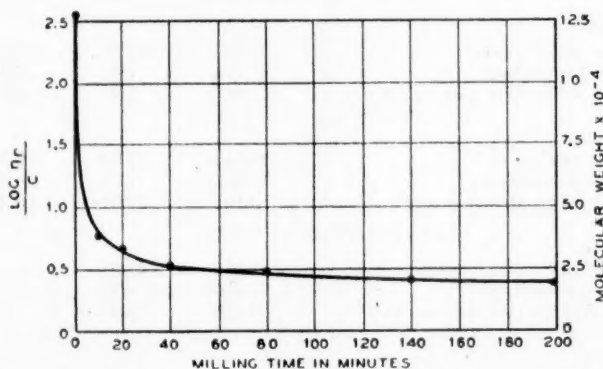


Fig. 8.—Effect of milling time at 95° F. on viscosity index and molecular weight of pale crepe.

tional stearic acid was added to each fraction to replace that removed by fractionation. Exhaustive acetone and chloroform extraction was made to show the lack of cross-linking of the low polymers during vulcanization, as indicated by the amount of polymer extractable with chloroform. In Table

XI and XIII the pure gum vulcanizates (12, 13, and 14) are compared, using the original Buna-S and its high- and low-molecular-weight fractions. These results show that the presence of the low-molecular-weight portion of Buna-S decreases modulus and tensile strength and increases chloroform extract. The amount of chloroform extract, based on the polymer, is somewhat less when carbon black is present. This may be due in part to the higher content of sulfur present in the tread stock. These data are plotted in Figures 5, 6, and 7.

EFFECT OF MILLING CREPE RUBBER

High-, medium-, and low-molecular-weight rubbers were prepared by milling pale crepe 3 minutes at 212° F, 10 minutes at 95° F, and 200 minutes at 95° F, respectively. The average molecular weights, determined by the viscosity procedure⁶, were 62,000, 32,000, and 20,000, respectively. Compounds were also prepared by using a 50-50 mixture of high- and low-molecular-weight rubber. Effect of milling time on viscosity index and molecular weight of pale crepe is shown in Figure 8.

TABLE XIV
DATA ON PURE GUM CREPE RUBBER STOCKS

Compound no.	15	16	17	18
A. Crepe (62,000 mol. wt.)	100
B. Crepe (32,000 mol. wt.)	...	100
C. Crepe (20,000 mol. wt.)	100	...
D. 50A + 50B	100
Zinc oxide XX-72	10	10	10	10
Stearic acid	2	2	2	2
Sulfur	3	3	3	3
808	0.75	0.75	0.75	0.75
Tetramethylthiuram monosulfide	0.10	0.10	0.10	0.10
Neozone-A	1	1	1	1
Curing temp. (° F)	287	287	287	287
10-minute cure				
Tensile (lbs. per sq. in.)	5185	4775	3935	4070
Elongation (percentage)	775	790	830	735
Modulus at 500% (lbs. per sq. in.)	915	760	515	810
20-minute cure				
Tensile (lbs. per sq. in.)	4830	4770	3930	4290
Elongation (percentage)	685	715	670	705
Modulus at 500% (lbs. per sq. in.)	1465	1280	1250	1250
30-minute cure				
Tensile (lbs. per sq. in.)	4175	4340
Elongation (percentage)	650	660
Modulus at 500% (lbs. per sq. in.)	1550	1680
40-minute cure				
Tensile (lbs. per sq. in.)	4160	4050
Elongation (percentage)	640	650
Modulus at 500% (lbs. per sq. in.)	1540	1680
Hardness (Shore A, 20 min.)	43	43	38	43
Acetone extract (percentage)	5.85	6.28	6.28	5.87
Chloroform extract* (percentage)	0.77	0.75	1.15	0.90

* Chloroform extracts were partly crystalline

The data on pure-gum stocks are given in Table XIV and on tread stocks in Table XV; they are plotted in Figures 9, 10, and 11. The effect of physical properties on reducing the molecular weight of crepe by excessive milling is not so pronounced as is shown by the high and low fractions of Buna-S. The same is true for tread stocks 19 and 20. The low-chloroform extracts found in the natural rubber compounds along with their superior physical properties is evidence that natural rubber is more effectively cross-linked than Buna-S during vulcanization.

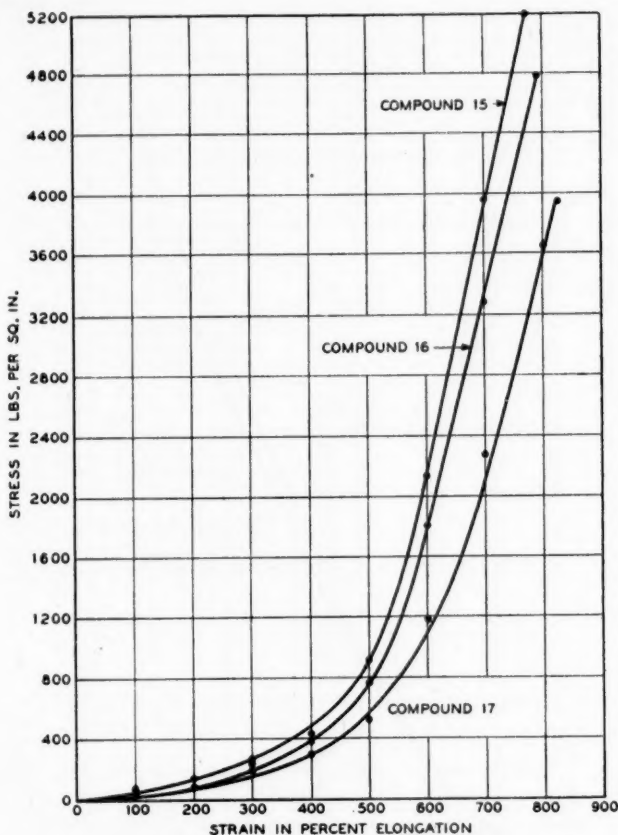


FIG. 9.—Stress-strain curves of pale crepe pure-gum compounds made with rubber of different molecular weights.

EFFECT OF MIXING RUBBER AND GUTTA-PERCHA

By mixing crepe rubber and leaf gutta-percha hydrocarbon BR-19 from the Tjipetir, Java, plantation, it was thought that crystallization of each hydrocarbon would be inhibited. Rubber hydrocarbon having the *cis* configuration would not so readily form crystals in the presence of gutta-percha which has the *trans* configuration. The object was not to prevent crystallization of the gutta and rubber entirely, but to reduce it considerably. The compositions and test data are given in Table XVI. The sulfur-accelerator combination

was selected after the preparation and evaluation of numerous preliminary compounds. The gutta was presoftened in water at 195° F, and the mill rolls were maintained at this temperature. Compound 24 was prepared by blending equal weights of compounds 22 and 23. Compound 21 served as blank. The best cures (plotted in Figure 12) show that the mixing of *cis* and *trans* isomers results in a somewhat lowered tensile strength which is very sensitive

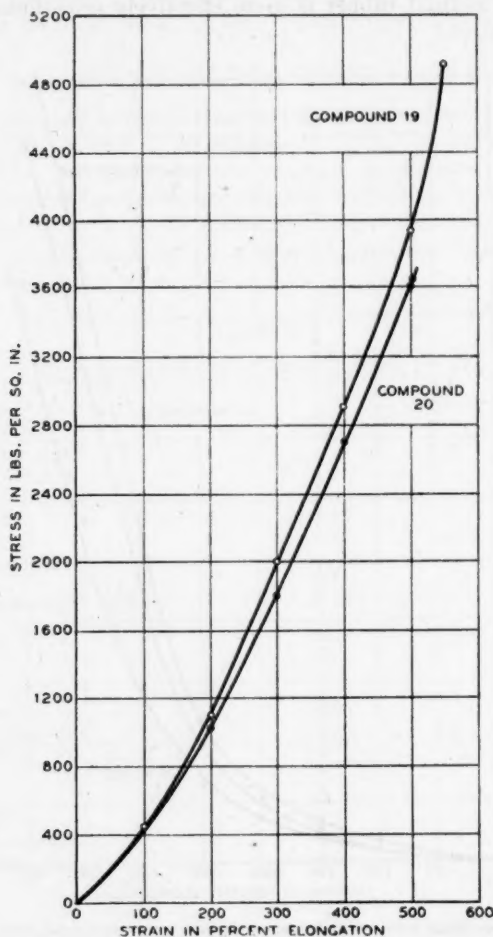


FIG. 10.—Stress-strain curves of pale crepe tread compounds, cured 40 minutes at 287° F.

to overcure. It is not certain, therefore, whether this lowering is a structural effect or due to failure to find best cure.

The importance of crystallization as a factor in contributing to strength is indicated in the greatly reduced strength shown by compound 24 in the uncured state. In this case the gutta hydrocarbon loses over 70 per cent of its strength when mixed with an equal amount of lightly milled rubber. When vulcanized, this mixture increases in strength to about 90 per cent of that of the original vulcanized whole gutta or whole rubber, since the cross-linking of

TABLE XV
DATA ON CREPE RUBBER TREAD STOCKS

Compound no.	19	20
Crepe (62,000 mol. wt.)	100	...
Crepe (20,000 mol. wt.)	...	100
Neozone-D	1	1
Mercaptobenzothiazole	1.50	1.50
Kosmobile-77	50.00	50.00
Zinc oxide XX-72	5.00	5.00
Stearic acid	3.00	3.00
Sulfur	3.00	3.00
Curing temp. (° F)	287	287
20-minute cure		
Tensile (lbs. per sq. in.)	4280	2935
Elongation (percentage)	655	500
Modulus at 300% (lbs. per sq. in.)	1210	1350
40-minute cure		
Tensile (lbs. per sq. in.)	4910	3645
Elongation (percentage)	560	505
Modulus at 300% (lbs. per sq. in.)	2000	1840
60-minute cure		
Tensile (lbs. per sq. in.)	4730	3400
Elongation (percentage)	555	455
Modulus at 300% (lbs. per sq. in.)	2050	2030
80-minute cure		
Tensile (lbs. per sq. in.)	4600	3340
Elongation (percentage)	520	420
Modulus at 300% (lbs. per sq. in.)	2180	2120
Hardness (Shore A, 40-min.)	65	65
Acetone extract (percentage)	4.7	4.8
Chloroform extract (percentage)	0.84	1.22

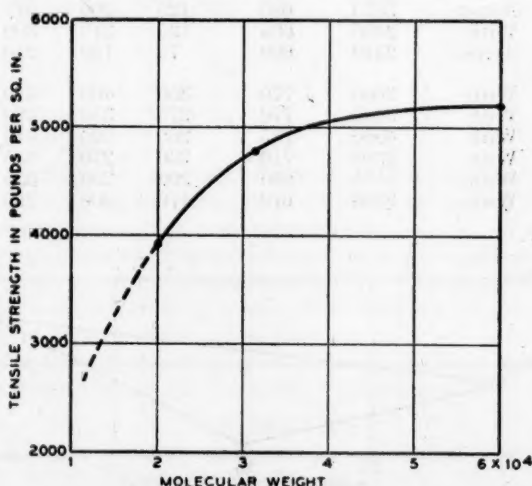


FIG. 11.—Tensile strength of pale crepe pure-gum compounds vs. molecular weight.

TABLE XVI
DATA ON RUBBER—GUTTA-PERCHA STOCKS

Compound no.		21	22	23	24
Gutta BR-19		100	100	...	50
Crepe rubber		100	50
Neozone-A		1	1	1	1
Sulfur		...	3	3	3
Zinc oxide (Kadox B.L.)		...	10	10	10
Stearic acid		...	2	2	2
808		...	0.75	0.75	0.75
Tetramethylthiuram monosulfide		...	0.10	0.10	0.10

Compound no.	Cure at 287° F. (min.)	Direction of grain	Tensile (lbs. per sq. in.)	Elongation (percentage)	Modulus (lbs. per sq. in.)				
					100%	200%	300%	400%	500%
21	Uncured	With Across	4475	350	1800	2200	3100
			4000	410	1800	2200	3100
22	Uncured	With	4040	425	1900	2125	2900	3800	...
		Across	3675	400	1500	1650	2600
	10	With	3985	505	750	1000	1975	2900	...
		Across	4600	540	875	1150	2150	3050	4000
	15	With	4355	540	700	950	1950	3050	3875
		Across	4335	540	700	950	1950	3000	3850
	20	With	3970	480	600	1000	1900	3100	...
		Across	4110	515	625	825	1775	3900	...
23	10	With	4875	730	75	175	300	475	1025
		Across	4600	800	75	125	200	325	625
	15	With	4725	720	75	200	300	550	1200
		Across	4910	725	75	200	300	500	1050
	20	With	4800	675	110	225	400	700	1550
		Across	4640	680	100	225	375	625	1400
24	Uncured	With	1200	50
		Across	520	140	425
	10	With	3075	675	200	250	350	600	1100
		Across	3075	685	125	200	275	475	975
	15	With	2400	605	125	210	300	475	1100
		Across	2310	600	75	150	250	475	1050
24	4*	With	3600	770	350	400	450	750	1300
	6*	With	3640	770	275	350	430	640	1230
	8*	With	4060	785	265	320	415	630	1210
	10*	With	3395	710	230	270	335	560	1150
	12*	With	3155	680	200	250	320	560	1120
	14*	With	2980	670	170	200	265	430	830

* Cured at 274° F.

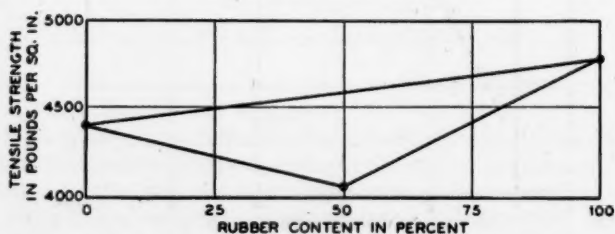


Fig. 12.—Effect of mixing *cis* and *trans* polyprene isomers on tensile properties.

the rubber has served to prevent its flow. The vulcanized gutta loses most of its strength when heated at 140–200° F. At the higher temperatures it becomes very short and tender, and is similar to vulcanized pure gum Buna-S in strength and general appearance. Vulcanized pure gum rubber, on the other hand, retains a large part of its strength at these elevated temperatures. Since vulcanized rubber crystallizes on stretching, the importance of crystal reinforcement on the strength of polymers is indicated.

Gutta or balata hydrocarbons change permanently to a rubberlike vulcanizate when cured under certain conditions. Table XVII shows conversion of

TABLE XVII
DATA ON BALATA COMPOUNDS

Compound no.	25	26
Balata hydrocarbon	94	96.5
Sulfur	5	2.5
Zinc butylxanthate	1	1.0
Curing temp. (° F)	287	287
0.5-hour cure		
Tensile (lbs. per sq. in.)	3920	3945
Elongation (percentage)	480	445
Permanent set	245	250
1-hour cure		
Tensile (lbs. per sq. in.)	3465	3615
Elongation (percentage)	515	440
Permanent set	225	245
2-hour cure		
Tensile (lbs. per sq. in.)	3125	3330
Elongation (percentage)	570	470
Permanent set	155	230
3-hour cure		
Tensile (lbs. per sq. in.)	2440	3385
Elongation (percentage)	635	520
Permanent set	25	206
17-hour cure		
Tensile (lbs. per sq. in.)	1685
Elongation (percentage)	...	550
Permanent set	...	10

balata to an elastomer as a result of curing over a long period. The corresponding reduction in tensile strength is a further indication that the effect is the result of reducing the degree of crystallization.

The nature and extent of cross-linking is also an important factor in contributing to tensile strength and elastic quality. Although only a few cross links are effective in eliminating plastic flow, tensile strength is probably not enhanced greatly by cross-links unless they are sufficient in number and properly placed in the three-dimensional gel structure. In other words, the strength of a structure is determined by that of its weakest member.

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THE DEPENDENCE OF DAMPING AND DYNAMIC MODULUS ON TEMPERATURE AS A MEANS OF EVALUATING THE ELASTIC BEHAVIOR OF RAW AND VULCANIZED RUBBER

THE DYNAMIC RESISTANCE OF SOFT RUBBER TO COLD *

H. ROELIG

DAMPING AS A MEASURE OF QUALITY

Measurements of damping as a criterion of the elastic behavior of soft rubber subjected to dynamic stresses (usually under pressure) have in recent years found general favor in the testing of soft-rubber products. As a basis for determining the damping effect, the familiar damping or hysteresis loop which is obtained by changing the load on a soft-rubber sample at a definite rate is the method most commonly used.

The area of this damping loop serves as a measure of the loss of energy (damping loss) which occurs during one complete cycle of strain and recovery. This is the *absolute damping*. However, rubber technologists are interested not only in this absolute value, but also in the closely related subject of a comparison of the damping loss with the total energy transformed by the rubber sample, i.e., with the work expended on the sample. In this way, an energy balance of the material in question is obtained. The best method is to calculate the damping as a percentage of the total work expended, and to express it as the ratio of the area of the hysteresis loop (Figure 1a) to the area which is bounded by the load curve (the upper part of the hysteresis loop), the total load ordinate, and the total elongation abscissa. This ratio may be designated as the *percentage damping*.

Still another definition of damping which is of interest technically in connection with vibration problems has been proposed by Lehr¹. In this case the area of the damping or hysteresis loop is related to the energy expended by a spring with no damping effect in completing a half cycle, as represented by the hatched triangular area in Figure 1b. The ratio of these two surface areas is designated by Lehr as the *damping factor*. If the percentage damping and the damping factor ψ are calculated from the damping loops obtained experimentally, the relation shown in Figure 2 is obtained. This diagram shows also the factor ψ/D , with which (assuming the damping loop to be elliptical) the percentage damping must be multiplied to obtain the damping factor.

For very small absolute damping losses and thus for small percentage damping values, this factor ψ/D is approximately 4. With greater damping losses it increases, and at a percentage damping of 60 per cent, for example, it reaches a value of 5.7.

In general the measurements show that damping is strongly influenced by temperature. The next problem was, therefore, to establish on a more exact

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 19, pages 47-49, June-July 1943.

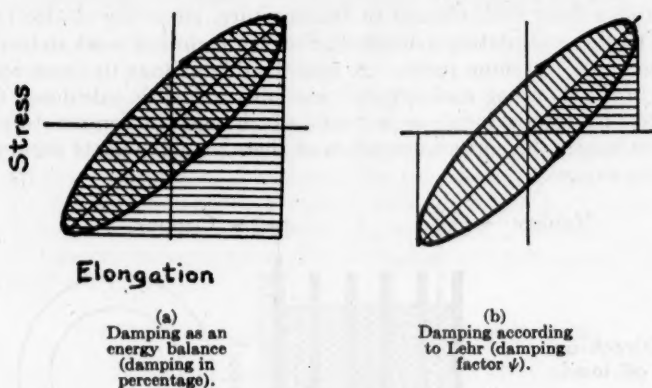


FIG. 1.—Definition of damping of a material.

basis the relation between damping and temperature. Knowledge of this relation is of great practical importance in three respects.

1. For the tire technologist to draw any conclusions regarding the internal heat build-up for different external temperatures and for different running speeds of the tire, it is necessary that data be available on the damping effect in the technically important temperature range of -40°C to 150°C . It is very desirable that the damping effect decrease with increase in temperature, as happens with many vulcanizates, since this tends to counteract the increase in temperature which occurs with increase in the revolutions per minute of the tire.

2. In contrast to this, the technologist who is concerned with vibration problems and who often desires high damping, *e.g.*, in torsional vibration dampers, wishes to obtain vulcanizates whose damping values change to the

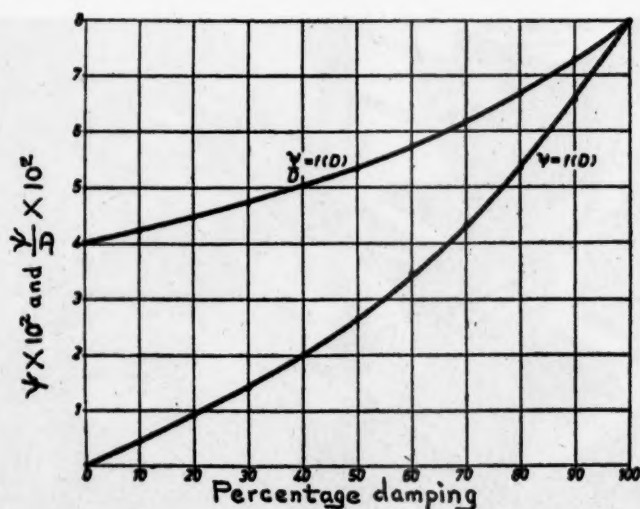


FIG. 2.—Relation between percentage damping and damping factor.

least possible extent with change in temperature, since the elastic constants which are used in calculating vibration effects in technical work determine the dimensions of the machine parts. A considerable change in these constants, especially in the damping and dynamic modulus (which is calculated from the slope of the hysteresis loop) as a result of changes in temperature, would therefore endanger the correct operation of these machine parts within certain temperature ranges.

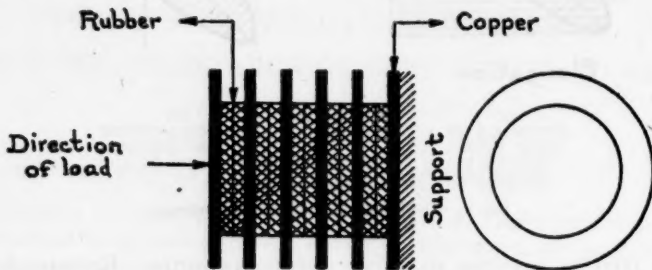


FIG. 3.—Assembly for measuring damping.

3. The conclusions which can be drawn regarding the structure of a polymer from the relation of the mechanical properties under static conditions (flow) and of the dielectric properties to the temperature suggest that conclusions regarding the structure of the polymer can be drawn also from the damping as a function of temperature. The damping losses under dynamic stress correspond to the electrical losses in an alternating field, and are comparable to the elastic aftereffect (erroneously described as flow in the case of rubber) under static stress. In all three cases curves are obtained from which conclusions can be drawn regarding the distribution of the times of relaxation of mechanical and electrical systems under stress.

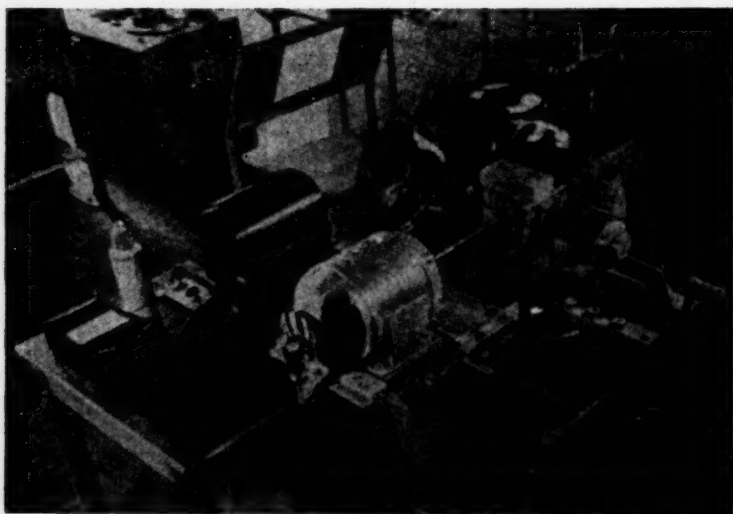


FIG. 4.

APPARATUS FOR MAKING THE MEASUREMENTS

The apparatus which was used to determine percentage damping has already been described in the literature². The same equipment used in this previous work was in principle again used but, in place of the solid cylindrical test-specimens which were used previously, 7×6 mm. Schopper discs were packed together, with larger copper discs placed between them (see Figure 3). In this way a uniform distribution of temperature was attained, and by heating or cooling the testing chamber the rubber samples could be maintained at a uniform temperature. Figure 4 shows the assembly, including the vibratory mechanism, the luminescent screen for recording the results, and the device for controlling the temperature.

TECHNIQUE OF MAKING MEASUREMENTS

If a series of damping loops for the particular sample of soft rubber in question is drawn, preferably beginning at a very low temperature, it is found

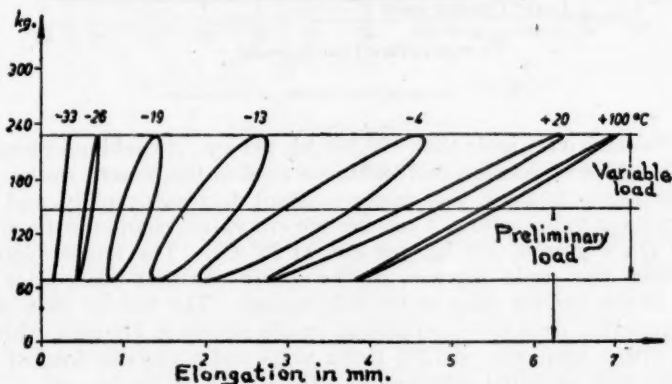


Fig. 5.—Damping and dynamic elastic constant as a function of temperature.

that these loops change greatly in character with increase in temperature (see Figure 5). A temperature is finally reached at which the damping cycles are no longer appreciably looped, but form a straight line, at which temperature damping becomes inappreciable, *i.e.*, reaches an extremely low value. It is possible, then, to speak of a dynamically determined *freezing temperature*. With increase in the temperature above this point, damping loops appear, *i.e.*, the rubber thaws. With further increase in temperature, damping increases very rapidly, and may, as is shown by the case illustrated in Figure 5, reach values as high as 62 per cent (see Figure 6). Finally a maximum damping value is reached, and this, together with the temperature at which the maximum occurs, serves to characterize any particular sample of soft rubber.

With a still further increase in temperature, damping decreases at first rapidly, then more slowly; hence it is especially advisable in tire engineering to study the damping effects at 0°, 20° and 100° C.

It has also been found that the inclination of the damping loops, from which the dynamic elastic constant or dynamic elastic modulus (E modulus) can be calculated, changes slightly. As long as the rubber sample remains in a frozen condition, the elastic constant is practically independent of tempera-

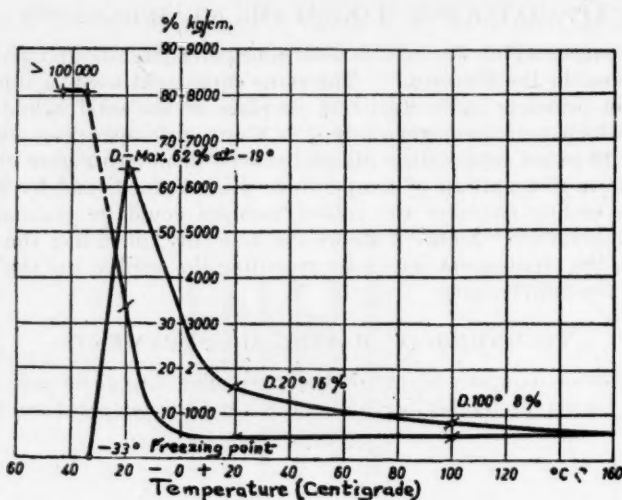


FIG. 6.—Damping as a function of temperature.

ture and, because it is higher than 100,000 kg. per cm., it could not be measured accurately by the equipment and technique used in the present work. But as the rubber begins to thaw, this elastic constant decreases rapidly, and at considerably higher temperatures it reaches the low values characteristic of rubber elasticity (In Figure 6, 480 kg. per cm. at 20° C). The temperature range within which this rapid decrease in the elastic constant takes place can be regarded as the *freezing range* of the soft rubber. The tabular data in Table 1 are summarized from the experimental results shown in Figure 6, which were obtained with a frequency of $12\frac{2}{3}$ Hertz units and a variable load of ± 6 kg. per sq. cm. with an initial compressive force of 11.5 kg. per sq. cm.

TABLE 1

	Temperature (Centigrade)	Damping (percentage)	Dynamic elastic constant (kg. per cm.)	Dynamic modulus (kg. per sq. cm.)
Freezing temperature	-33°	0	100,000	30,000
Maximum damping	-19°	62	2,700	860
	0°	32	560	178
	20°	16	480	153
	100°	8	550	175

PRACTICAL APPLICATION OF THE METHOD

The experimental results answer two important questions bearing on the application of the vibratory method to the study of soft-rubber products:

1. the behavior of vulcanizates when stressed dynamically at low temperatures; and
2. the serious losses in energy by the damping of tires in a temperature range which is of technical and practical importance.

Since various technically important factors, such as the type of rubber, plasticity of the raw rubber, composition of the rubber mixture, and state of vulcanization, influence the experimental results, a few examples are given to show the parts played by these factors.

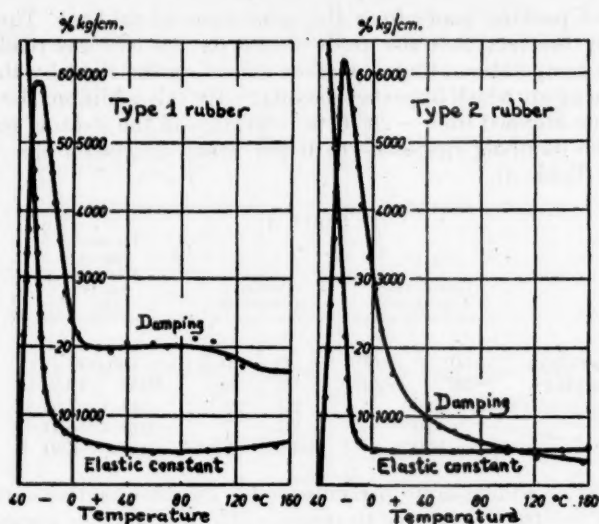


Fig. 7.—Damping and structure.

INFLUENCE OF THE TYPE OF RAW RUBBER

In addition to differences in behavior at low temperatures, different types of vulcanizable rubbers are most easily distinguished by differences in their temperature coefficients of damping between 0° and 100° C. Figure 7 shows the damping as a function of temperature for two different types of rubber (vulcanized but not loaded), which are characteristically different. Rubber of Type 1 is a type the damping of which changes only slightly between 5° C and 100° C. Vulcanizates of this character are desirable for applications involving vibration, where high damping is required. The tire technologist on the contrary prefers rubbers of the second type because, for the same processing and the same mechanical properties, a finished tire gives the best results when the damping losses of its structural parts decrease with increase in temperature so as to offset heat build-up at high speeds.

The results obtained with the two types of rubber are summarized in Table 2.

TABLE 2

Type of rubber	Temperature (centigrade)		Damping (percentage)		Dynamic elastic constant (kg. per cm.)		Dynamic compression modulus (kg. per sq. cm.)	
	1	2	1	2	1	2	1	2
Freezing temperature	-40°	-37°	0		100,000		30,000	
Maximum damping	-26°	-21°	58	62	3000	2300	947	732
	0°		23	29	660	490	222	156
	20°		20	14	550	490	175	156
	100°		21	5	490	500	156	159

INFLUENCE OF THE COMPOSITION OF THE MIXTURE

The influence of the composition of the mixture on the damping and on the dynamic elastic constant can be shown by other examples. Figure 8 compares

two grades of packing made from the same type of rubber. They are distinguished by the fact that the grade shown on the left was rendered more stable at low temperatures than the grade shown on the right by the addition of a softening agent which imparts elasticity. By this addition, the maximum damping value dropped from -20°C to -36°C , and the freezing temperature (at which the damping decreases to 0 per cent) dropped from -47°C to -60°C (see Table 3).

TABLE 3

Mixture	Temperature (Centigrade)		Damping (percentage)		Dynamic elastic constant (kg. per cm.)		Dynamic compression modulus (kg. per sq. cm.)	
	1	2	1	2	1	2	1	2
Freezing temperature	-60°	-47°	0	0	100,000		30,000	
Maximum damping	-36°	-20°	55	49	1800	1950	572	620
		0°	23	23	430	740	137	235
		20°	20	17	400	650	127	205
		100°	14	9	390	630	124	200

The effects of adding large percentages by weight of active carbon black, as is done in tire-tread mixtures to increase the resistance to abrasion and to tearing, are shown in Figure 9, in which a tire-carcass mixture and a tire-tread mixture made from the same type of rubber are compared. The higher loading of carbon black in the tire-tread mixture resulted in a considerable increase in the damping, which, for the particular type of rubber used, fluctuated around a value of 20 per cent between 0° and 100°C . In contrast to this, the damping of the tire-carcass mixture had a value around 12 per cent between 30° and 80° , which decreased to a value below 10 per cent when the temperature was above 120°C .

As was proved by numerous experiments, the higher loading of the tire-tread mixture led to a decrease in the maximum value of the damping, which

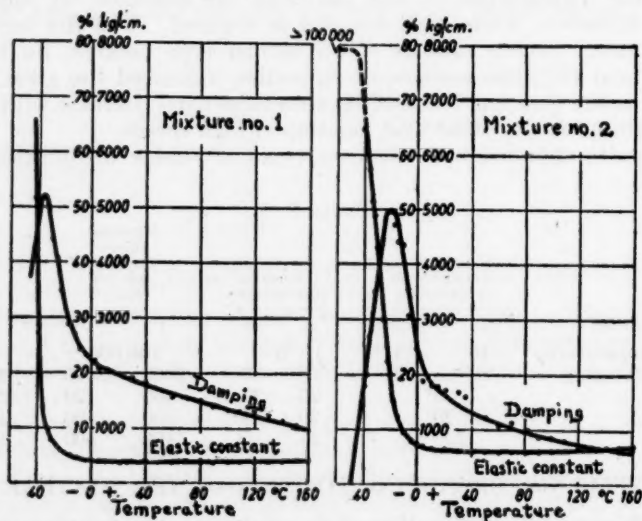


FIG. 8.—Damping and dynamic elastic constant as functions of temperature.

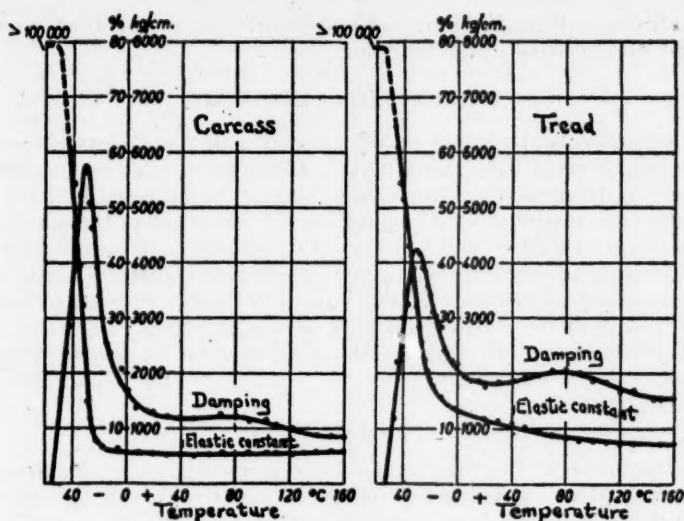


FIG. 9.—Damping and dynamic elastic constant as functions of temperature.

for the tire-tread mixture was found to be 42 per cent, compared with 57 per cent for the tire-carcass mixture. A further characteristic of heavily loaded rubber mixtures is the earlier beginning of the increase in the elastic constant as the temperature decreases. Whereas the dynamic elastic constant of the tire tread mixture began to increase from 120° C with decrease in temperature, the elastic constant of the tire-carcass mixture showed a similarly rapid increase only below -10° C.

TABLE 4

Mixture	Temperature (Centigrade)		Damping (percentage)		Dynamic electric constant (kg. per cm.)		Dynamic compression modulus (kg. per sq. cm.)	
	carcass	tread	carcass	tread	carcass	tread	carcass	tread
Freezing temperature	-53°	-51°	0°	0°	100,000		30,000	
Maximum damping	-30°	-30°	57	42	2700	3440	860	1090
		0°	11	21	610	1340	195	427
		20°	13	18	560	1180	178	376
		100°	11	20	610	770	194	245

INFLUENCE OF PLASTICITY OF THE RAW MIXTURE

A further problem is the influence of various factors concerned with the processing of rubber mixtures, such as plasticity, on the damping. With increase in plasticity, whether brought about by increased mastication or by thermal softening, it would be expected that the elastic aftereffect, and therefore the damping as well, would increase. However, these effects can be at least partially compensated for by adjustments of the percentages of sulfur and accelerator.

INFLUENCE OF VULCANIZATION

The influence of the state of vulcanization on the elasticity of soft-rubber vulcanizates can be demonstrated by damping measurements, *e.g.*, the rela-

tively high plasticity in the range of considerably uncured rubber mixtures is associated with relatively high damping.

INFLUENCE OF FREQUENCY

The experiments described in the present paper were carried out at a constant frequency of $16\frac{2}{3}$ Hertz units. If rubber is composed of structural elements with different relaxation times, it would be expected that the damping and dynamic modulus would depend on the frequency of the applied stress or, better, on the resultant acceleration. Preliminary experiments have shown that the freezing temperature of a given vulcanizate loaded statically is lower than the freezing temperature of the same vulcanizate stressed dynamically. The dependence of the elastic properties on the frequency of stressing will be reported after further changes in the experimental apparatus have been completed.

SUMMARY

The dependence of the damping and elastic modulus of a vulcanizate on its temperature makes it possible to evaluate its elastic behavior throughout the temperature range which is of technical importance.

Measurements were carried out at a constant frequency of $16\frac{2}{3}$ Hertz units (1) to determine the damping effect, in which case the freezing temperature of the vulcanizate, the maximum damping above the freezing point, and in many cases the decrease in damping with increase in temperature above 0°C , were determined, and (2) to determine the elastic modulus, in which case the freezing temperature of the vulcanizate, the freezing range, and the dynamic modulus of elasticity were determined.

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DAMPING, HEAT DEVELOPMENT AND THE LENGTH OF LIFE OF VULCANIZATES *

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In recent years dynamic testing methods have been used to an increasing extent in studying the elastic properties of vulcanized rubber. These dynamic methods, which are based on various principles and employ various types of apparatus¹, attempt to duplicate closely actual service conditions such as are encountered with automobile tires, rubber belts, rubber springs, etc. Test-specimens, usually of cylindrical form, are subjected to repeated stresses with frequencies of the order of 10-20 Hertz units, and the resulting energy losses are measured either directly or indirectly by the resulting increases in temperature. In addition to supplying data with which to judge quality on the basis of energy, it is possible from the information furnished by these dynamic methods to draw conclusions regarding the behavior of rubber products when deformed under various conditions. The so-called elastic constants and moduli, which can be measured experimentally, give useful data on methods of construction, and make it possible to estimate the deformation to be expected in service.

STATEMENT OF THE PROBLEM

Rubber can be regarded as the prototype of highly elastic materials. Even when it is deformed very greatly, it recovers its original form almost completely after the stress is released. This applies equally to tension, compression, shear and torsion. However, deformation is never completely reversible, nor is the work expended in deforming rubber completely recovered after the stress is removed. If A is the amount of work expended to obtain a certain deformation, the amount of energy recovered after release of the stress is $A - \Delta A$. In this case ΔA represents the *absolute damping*. If damping is represented as a proportion of the total work expended, this *percentage* or *relative damping*² is:

$$\psi = 100 \frac{\Delta A}{A} \text{ (in percentage)}$$

This percentage damping is an important constant of a material, and its value does not depend in any essential way on the experimental conditions³, e.g., on the form of the test-specimen. On the contrary, it does depend on the frequency of the stress applied⁴ and on the temperature⁵, as would be expected from theoretical considerations.

To make these relations quite clear, the causes of damping in rubberlike materials will be discussed in a brief way. Even rubber which contains no fillers shows a small amount of damping, an effect which may be attributed to

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 19, pages 55-58, August-September 1943.

internal friction. The shorter the time of deformation, the greater the proportion of this molecular friction which is manifest in the form of damping, *i.e.*, damping increases with increase in the frequency of the applied stress. In vulcanizates containing fillers, there is additional internal friction at the boundary surface of rubber and filler. With rise in temperature, the amount of damping caused by internal friction decreases. Types of rubber which are not sufficiently vulcanized to suppress plastic flow show, when subjected to dynamic stresses, the phenomena of flow to a relatively great extent, and deformation involves the expenditure of additional work which is irreversible. Flow, and the relative damping effect which is associated with it, increase with rise in temperature, and this increase in flow may be so great that in some cases the total damping of weakly vulcanized rubber actually increases with rise in temperature. For this reason different vulcanizates may, within a certain range of temperature, behave entirely differently, and it has recently been shown⁵ that the dependence of damping on temperature over a range from very low to very high temperatures gives valuable information on the quality and behavior of vulcanized rubber.

In the work to be described in the present paper, the reverse problem was attacked, *i.e.*, the increase in temperature of a vulcanizate which is caused by damping, and its resulting effect on the life of the vulcanizate.

It should be mentioned beforehand that treatment in an exact way of the relations between heat economy and behavior when deformed appears to be possible only if a sufficiently large quantity of material is evaluated by static methods, because the results naturally tend to show great deviations.

RISE IN TEMPERATURE OF TEST-SPECIMENS SUBJECTED TO DYNAMIC STRESSES

The energy loss ΔA , which is defined as the absolute damping, is manifest in the form of a corresponding amount of heat. If ΔA is expressed in mkg., each change in stress involves the formation of $(\Delta A)/427$ calories. This amount of heat raises the temperature of the rubber; in fact the temperature rise ϑ depends on the heat capacity C_w , where $C_w = Vsc$ (V is the volume, s the specific gravity, and c the specific heat). The rate of increase in temperature $d\vartheta/dt$ is then given by the following relation⁶:

$$\frac{d\vartheta}{dt} = \frac{(\Delta A)n}{427 Vsc} \quad (1)$$

where n is the number of changes of the load per second.

On the other hand, a rubber test-specimen gives off heat to the surrounding medium. The resulting fall in temperature can be expressed by the relation:

$$\frac{d\vartheta}{dt} = -k \cdot \alpha \quad (2)$$

where k is a constant which depends on the dimensions of the test-specimen and on the heat loss at the boundary surface, and α is the temperature factor.

As is known, the rise in temperature which occurs during the period when a test-specimen is stressed dynamically tends toward a limiting value $\vartheta_{\max.}$. This limiting value is reached when the rate of increase in temperature and the rate of heat loss are equal. By combining Equations (1) and (2), the ex-

pression:

$$\vartheta_{\max.} = \frac{(\Delta A)n}{427 V sck \cdot \alpha} \quad (3)$$

is obtained.

If the dimensions of the test-specimen are regarded as constant, *i.e.*, if V and k are equal, then the maximum rise in temperature is directly proportional to the absolute damping and to the frequency, and inversely proportional to the heat conductivity λ (since $\lambda = \alpha \cdot s \cdot c$).

The validity of the relation shown above was confirmed by a large mass of experimental data. Figure 1, for example, shows the relation between abso-

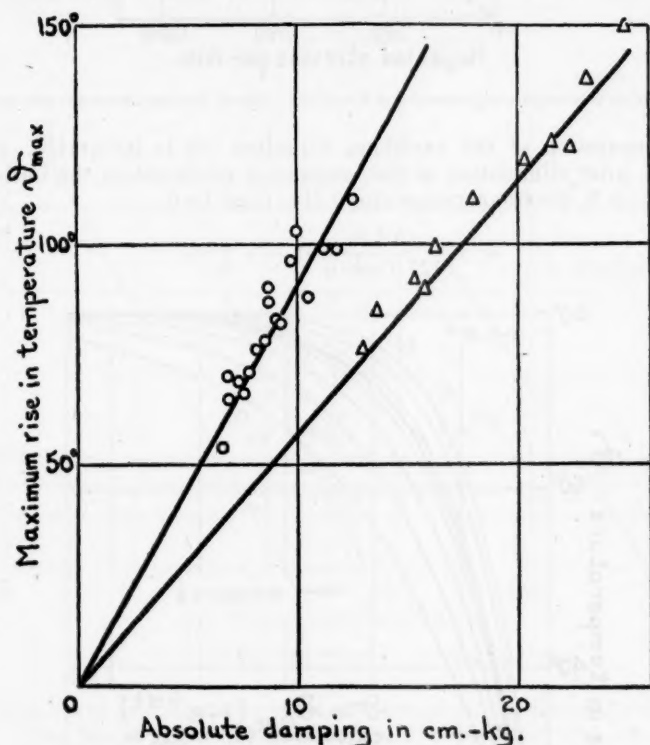


Fig. 1.—Relation between damping loss and maximum temperature. (Solid lines are calculated by Equation (3).)

lute damping and the maximum rise in temperature obtained with the damping apparatus described by Roelig³. Two representative shapes of test-specimen were chosen, and the experimental data were compared with the calculated result. The relation between maximum temperature and frequency⁷ is shown in Figure 2.

The dependence of the rise in temperature on time is made clear by combining Equations (1) and (2) in the following way:

$$\frac{d\vartheta}{dt} = \frac{(\Delta A)n}{427 V sck} - k \cdot \alpha \cdot \vartheta \quad (4)$$

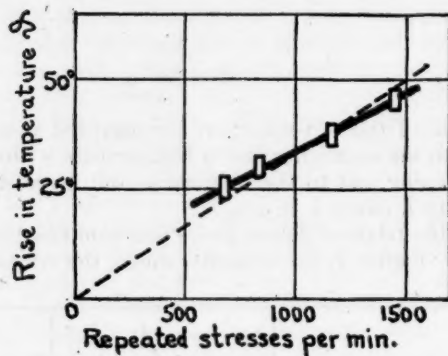


Fig. 2.—Rise in temperature as a function of frequency. (From Mackay, Anderson and Gardner.)

After separation of the variables, Equation (3) is integrated, with the result that, after elimination of the integration constants of the initial state, when time t is 0, the temperature rise ϑ also must be 0:

$$\vartheta = \frac{(\Delta A)n}{427 V sck \cdot \alpha} (1 - e^{-k \cdot \alpha \cdot t}) \quad (5)$$

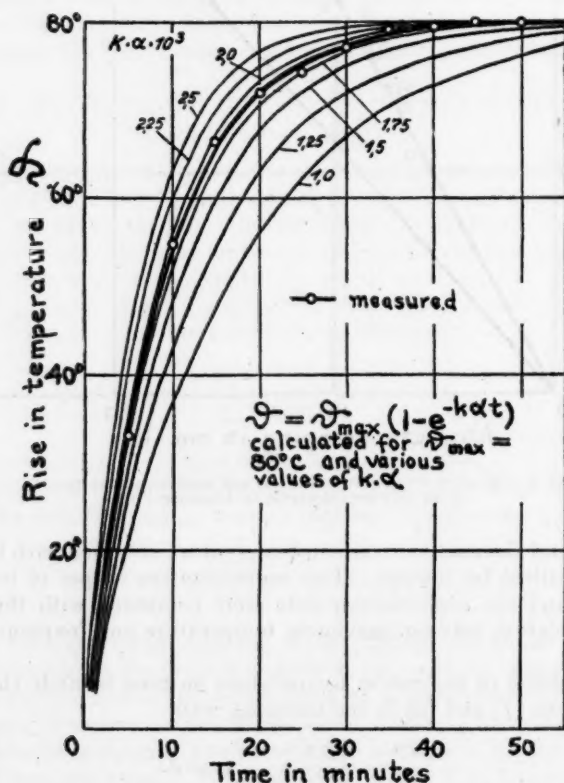


Fig. 3.—Rise in temperature during a vibration experiment.

or, if Equation (3) is incorporated in Equation (5):

$$\vartheta = \vartheta_{\max} \cdot (1 - e^{-k \cdot \alpha \cdot t}) \quad (6)$$

Figure 3 shows curves which are calculated from Equation (6) for various values of $k \cdot \alpha$ and are compared with a curve representing the rises in temperature determined experimentally.

For short periods of time, the e exponent can be expanded in a series, which can be disregarded beyond the first member of the series. By this artifice it is possible to obtain an approximate expression of the following form, in which no factor representing the heat loss is present⁸:

$$\vartheta = \frac{(\Delta A)nt}{427 V_{sc}} \quad (\text{for small values of } t) \quad (7)$$

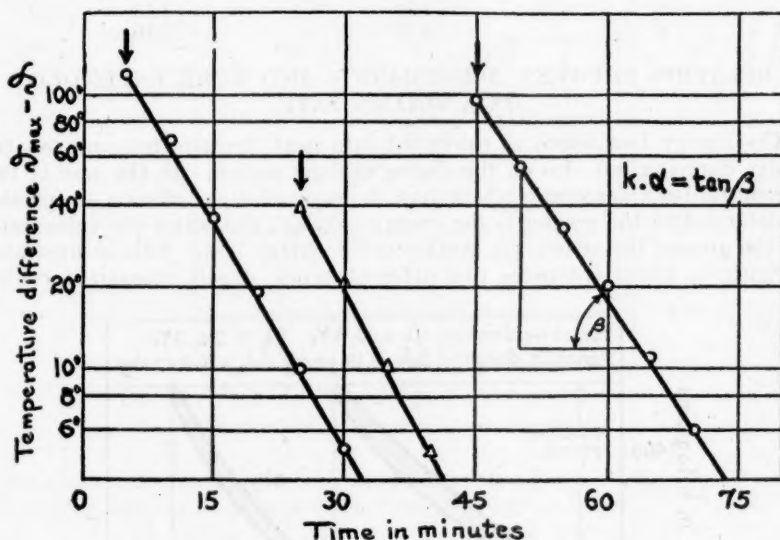


FIG. 4.—Changes in temperature during a vibration experiment.

To evaluate the temperature curves, knowledge of the thermal constants is essential. The temperature measurements are carried out with the aid of a copper-constantan thermoelement, which is imbedded in the test-specimen plied up from sheets in such a way that the junction is in the middle of the test-specimen. The specific heat is determined in a simple mixing calorimeter⁹ or, together with the heat conductivity, in a steam calorimeter¹⁰. The dimensional constant k can be calculated for definite conditions of heat loss (complete contact with steam)¹⁰. On the other hand, in measuring damping, the cylindrical test-specimen is in contact at the jacket surface with the outside air, yet at the same time on both circular surfaces is in contact with the highly conductive metal plates of the apparatus. The heat loss decreases, therefore, from the top, so the k constant must be determined experimentally. In contrast to a calculated k constant of 1.47 for a certain form of sample, a strictly practical k constant of 1.6 can be assumed.

Based on this k value of 1.6, a vibration experiment can be utilized for

determining the temperature factor. The product $k \cdot \alpha$ is easily obtained by determining the slope of the straight line obtained by plotting $\log (\vartheta_{\max} - \vartheta)$ against t (see Figure 4). In this way the α temperature factor values were calculated from the k constant of 1.6 and were compared with the α values determined experimentally.

TABLE I
COMPARISON OF TEMPERATURE FACTORS CALCULATED FROM DAMPING MEASUREMENTS WITH VALUES OBTAINED EXPERIMENTALLY

Sample	α Value calculated from damping	α Value obtained by direct measurement
1	1.37	1.33
2	1.12	1.20
3	1.20	1.22
4	1.14	1.15
5	1.20	1.15
6	1.92	2.10

RELATION BETWEEN DEFORMATION AND WORK EXPENDED ON A VULCANIZATE

The energy loss which is converted into heat depends not only on the relative damping but also on the degree of deformation. In the case of two different rubber vulcanizates which show the same relative damping, the greater the deformation the greater is the energy loss, i.e., the softer the vulcanizate and the greater the stress, the greater is the energy loss. This is illustrated in Figure 5, which compares two different types of soft vulcanized rubber

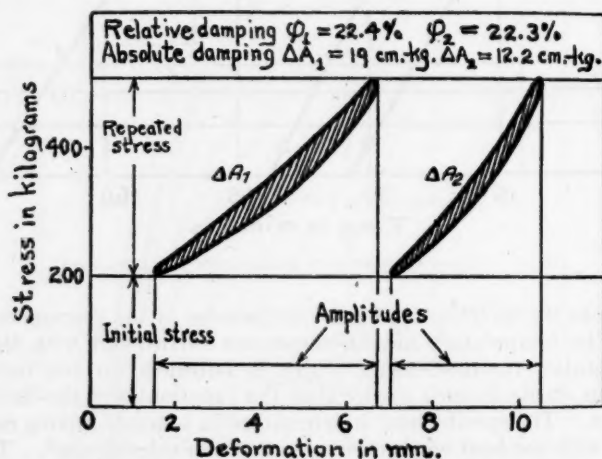


Fig. 5.—Comparison between two types of vulcanizates with the same relative damping for the same repeated stress.

having the same relative damping properties, but which, when subjected to the same repeated stress, show hysteresis loops with different areas.

Deformation under dynamic stressing can be expressed by the *dynamic elastic constant*, which is defined as that force which deforms the test-specimen 1 cm. Only for elastic materials which follow Hooke's law is this elastic constant invariable through the whole range of deformation. For rubberlike

materials in general, deformation is not proportional to stress, and the deformation curve represents a complex mathematical function. According to definition, the dynamic elastic constant represents the first derivative of the deformation. Therefore it changes through the entire range of deformation, and hence the state of deformation must in some cases be specifically defined¹¹.

In practice the dynamic elastic constant is determined as a mean value from experimental data on vibration, in which case the bend in the curve is disregarded (see Figure 6). If the amplitude is small enough, this mean value

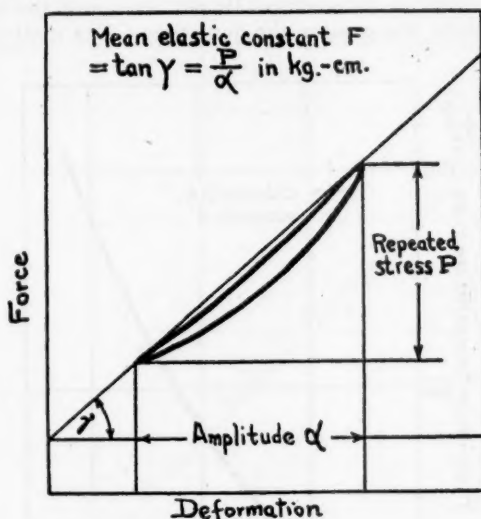


FIG. 6.—Determination of mean elastic constants.

of the elastic constant can be used without great error in further calculations. The energy loss can be calculated in a simple way¹².

$$\Delta A = \frac{P^2}{200 F} \cdot \varphi \quad (8)$$

when based on a predetermined stress, and

$$\Delta A = \frac{F \cdot a^2}{200} \cdot \varphi \quad (9)$$

when based on a predetermined deformation, where P is the stress, F is the elastic constant, and a is the amplitude.

With respect to the evolution of heat, the behavior of any type of vulcanized rubber depends on whether it is stressed repeatedly under a constant load or to a constant deformation.

The quadratic relation between stress and energy loss, which finds its expression in the maximum temperature attained, can also be confirmed experimentally. Figure 7 shows a curve calculated from Equation (8), and the corresponding points determined experimentally. Equation (8) shows that, when both the stress and the relative damping are constant, the higher the

elastic constant, the better the thermal properties of a vulcanizate. This fact has been utilized for a long time in the construction of solid tires.

As already mentioned, Equations (8) and (9) are correct in only an approximate way, because they do not take into account the bend in the deformation curve. Disregarding erratic values, the calculated values are in general higher than the experimental values, and the deviations are not the same because of the changing concavity of the curve. To prove this, a comparison was made, with the aid of a large amount of experimental data, between the calculated and experimental values of the damping of a typical vulcanizate (see Figure 8). The deviations amount to as much as 10 per cent, and the softer and more supple the vulcanizate, the greater the deviation. The method is sufficiently

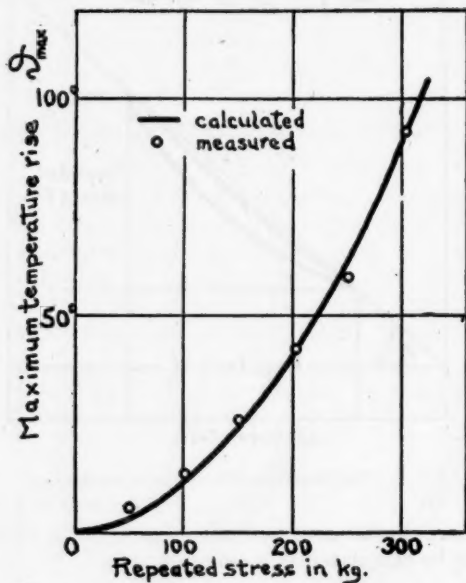


FIG. 7.—Maximum rise in temperature as a function of the repeated stress which is applied (Tire tread vulcanizate.)

precise, however, to find use as a check test in evaluating damping loops correctly. It might even be possible, with the aid of Equations (8) and (9), to evaluate experimental products which do not lend themselves to direct damping measurements¹³.

RELATIONSHIPS WITH THE LENGTH OF LIFE OF VULCANIZATES

When a test-specimen is subjected to a repeated stress over a long period of time, its length of life depends on the magnitude of the stress, and this life can be expressed in terms of the number of times the stress is applied. There is a limiting range of stresses below which the resistance of the vulcanizate to repeated stressing becomes so great that the length of life of the test-specimen becomes practically unlimited. If stress is plotted against length of life (expressed as number of stresses), so-called Wöhler curves are obtained. Such curves have become of great importance in evaluating the properties of various

industrial materials. Figure 9 shows typical Wöhler curves of two different types of vulcanized rubber. In plotting lengths of life, which deviate greatly, particularly with vulcanized rubber, and which therefore should be based on a large number of measurements, it is customary to use a logarithmic scale so as to be able to represent graphically the highest values, which may reach several powers of 10. In some cases the logarithm of the number of stresses is useful as an index of quality. The logarithmic method of plotting has also been recommended for the evaluation of resistance to cracking on bending¹⁴.

The destructive effect of dynamic stressing can be ascribed to several essentially different phenomena. In the first place heat is developed during stress-

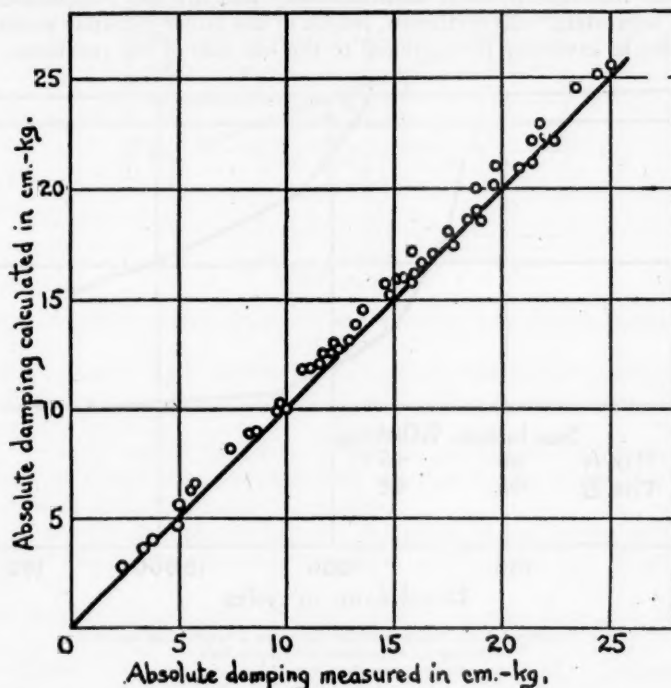


FIG. 8.—Comparison of the damping energy calculated by Equation (8) with that determined experimentally.

ing, as a result of which there is a rise in temperature. This higher temperature in turn starts various chemical reactions, or at least accelerates them. As a result of oxidation, aftervulcanization, polymerization or depolymerization, such deep-seated changes may take place in a vulcanizate that its structure is finally broken down. Fatigue, cracking, disintegration or internal cavities or channels are some of the phenomena which indicate these destructive structural changes. The differing resistance of various types of vulcanizates to break down from these effects is attributable primarily to the retardation of these destructive chemical reactions. For instance, antioxidants have a favorable effect on the length of life of natural-rubber vulcanizates, because by this means the oxidative depolymerization brought about by atmospheric oxygen is retarded¹⁵.

In addition to these reactions, which are controlled above all else by the prevailing temperature, recent knowledge based on theoretical considerations points to structural changes brought about solely by the action of external mechanical forces¹⁶. It would be expected that these effects would not be influenced by the temperature, but in any case the chemical effects are for the most part predominant, for the mechanical forces necessary to bring about changes in molecular structure are necessarily very great, and probably are not encountered in ordinary tests of the resistance of vulcanizates to repeated stressing.

Direct measurement of the rates of these reactions is not possible, because the various reactions proceed simultaneously and are too complicated to be analyzed separately. Nevertheless, length of life under dynamic stressing can be regarded as inversely proportional to the net rate of the reactions. There

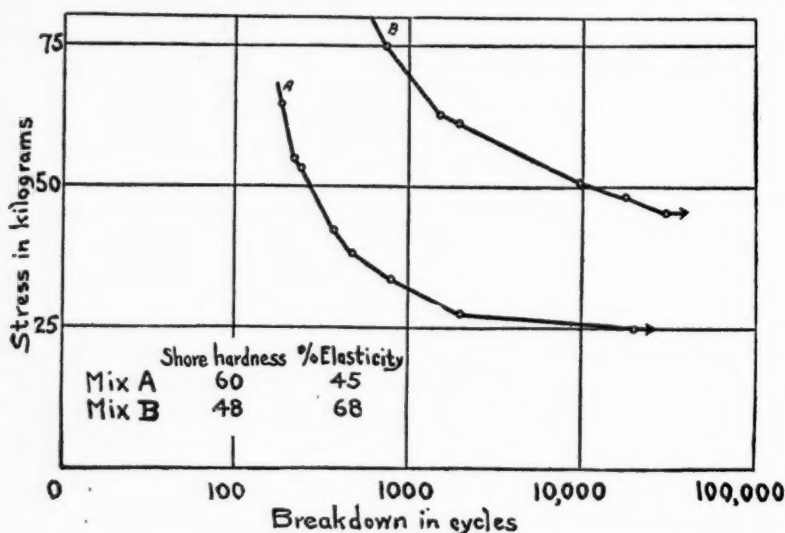


FIG. 9.—Breakdown value (Wöhler curve) as a function of the stress.
(Schopper apparatus with 3-cm. ball.)

must, therefore, be a relation between the length of life L and the temperature which follows the Arrhenius law for rates of reactions, *i.e.*, L is proportional to $e^{E/(RT)}$, where E is the energy of activation, R is the gas constant, and T is the absolute temperature. If this relation is expressed logarithmically, an equation already derived¹ is obtained:

$$\log L = e + f/T \quad (10)$$

where e and f are constants.

When temperatures are plotted against length of life in the reciprocal logarithmic system, straight lines are obtained, as exemplified in Figure 10¹⁷. From the slope of such a line it is possible to calculate both the activation energy of the destructive reaction and its temperature coefficient. Based on earlier experiments¹ and also on the data in Figure 10, the temperature coefficient lies between 1.4 and 1.7. A somewhat higher value for the temperature coefficient, *viz.*, 1.8, has been reported by Gough and Parkinson¹⁸. These

investigators also give an approximate equation, similar to Equation (10), for the relation between temperature and length of life:

$$\log L = e' - f'T \quad (11)$$

For the very small temperature range (100–120° C) studied by Gough and Parkinson, the experimental results conform to Equation (11). However, this equation does not agree with the actual relations sufficiently well for a broader

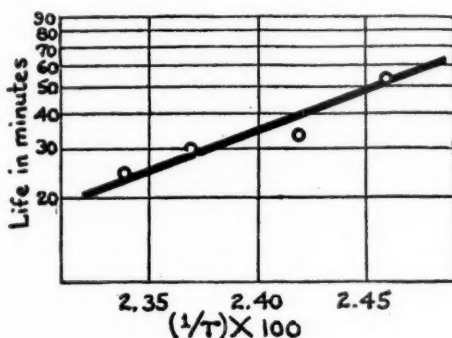


Fig. 10.—Relation between length of life and temperature developed (from Roberts¹⁷).

temperature range. It is interesting to compare the temperature coefficients discussed above with the temperature coefficients of the various individual reactions (see Table 2).

The low temperature coefficient of the destructive reaction indicates that there must be complicated interrelations between the individual partial reactions, probably including catalytic reactions.

Since further relationships between temperature and stress and between temperature and deformation corresponding to Equations (3), (8) and (9) can

TEMPERATURE COEFFICIENTS OF THE DESTRUCTIVE REACTIONS, AND OF THE INDIVIDUAL PARTIAL PROCESSES INVOLVED

Process	Temperature coefficient	Reference
Destruction	1.4–1.7	...
Destruction	1.8	Gough and Parkinson ¹⁸
Oxidation at 80° C	2.2 (approx.)	Morgan and Naunton ¹⁹
Degradation of Buna-S	2.2	Springer ²⁰
Polymerization of styrene	2.0–2.3	Springer ²¹
Vulcanization (based on sulfur consumed)	2.2–2.6	Twiss and Brazier ²²

be derived, it is possible that the length of life depends, at least in a qualitative way, on the stress and on the amplitude. It has been shown earlier¹ that $\log L$ is a simple function of the load, as is to be expected from theoretical considerations. The constantly recurring logarithmic function in measurements of the length of life of vulcanized rubber is in this way easily explained, and doubtless it would be easy to explain the Wöhler curves as well if a correspondingly greater amount of experimental material were available. It is suggested that similar investigations on the length of life of other industrial materials be carried out.

SUMMARY

Although it is still not possible to calculate or to predict the behavior and length of life of different types of rubber products under service conditions, it is nevertheless of value to make clear the relations involved, and to trace back the many already known phenomena to their physico-chemical causes. The present work deals with the following aspects of the subject.

A relation between damping, shape of test-specimen, heat conductivity, frequency and heat development is derived, with the aid of which both the rise in temperature and the maximum temperature, and in precise measurements the temperature factor as well, can be calculated.

With certain assumptions for the sake of simplicity, the energy loss can be calculated from the stress and elastic constant. It appears that the behavior of vulcanized rubber mixtures when they are tested under constant stress is different from that when they are tested at constant deformation.

The destructive action brought about by prolonged repeated stressing is ascribed to chemical reactions, and on the basis of this assumption it is shown that the length of life depends on the temperature. Attention is called to the possibility of evaluating Wöhler curves on a mathematical basis.

The equations which are formulated are verified by a large amount of experimental data, and a few characteristic diagrams are given by way of illustration.

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- ⁶ See Steinborn, "Die Dämpfung als Qualitätssatz für Gummi", Braunschweig, 1937, p. 13.
- ⁷ Mackay, Anderson and Gardner, *Trans. Inst. Rubber Ind.* 16, 123 (1940). Figure 2 does not show the required proportionality accurately, evidently because the energy losses decrease somewhat at higher frequencies in spite of the stress being the same.
- ⁸ Steinborn ("Die Dämpfung als Qualitätssatz für Gummi", Braunschweig, 1937) uses in his derivations only the initial tangent of the temperature rise, and does not go into further detail regarding heat losses.
- ⁹ See, for example, Kohlrausch-Krüger, "Kleiner Leitfaden der praktischen Physik", Leipzig and Berlin, 5th Ed., 1932, p. 166.
- ¹⁰ Gottwald, *Kunststoffe* 29, 248 (1939).
- ¹¹ An exact mathematical treatment of the deformation curve and of the elastic constant as a function of the deformation is very difficult. Up to the present time there have been various empirical or semiempirical equations, which for the most part apply only to part of the curve, and which contain constants having no definite physical meaning. In the course of the present author's investigations, which are concerned with the derivation of an elastic constant that does not depend on the dimensions of the test-specimen and degree of deformation, the problem of the mathematical treatment of the deformation curve was also touched upon. Judged by unpublished data and the form of the curve, an exponential function appears to be involved. The following relation exists between elastic constant and deformation:

$$\log F = pa + q$$
 where p and q are constants. From this the deformation curve is obtained by integration. This can in turn be utilized for the accurate determination of the energy loss. This derivation must, however, be verified in various respects. A detailed presentation of this problem is to appear in a later publication.
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EFFECT OF TEMPERATURE ON THE VIBRATION CHARACTERISTICS OF NATURAL AND SYNTHETIC RUBBERS *

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For many years we have considered climate as something not too important in connection with rubber compounds. As a rule we have used rubber without any temperature qualifications as far as the lower range of temperatures was concerned and have had very little real trouble. In the past three years, however, the situation has radically changed. For some time now a much larger part of our goods is being exposed to low temperatures because of the great development of the use of the airplane during the present war and the need of its use at high elevations where extreme cold exists and in temperatures such as those found in the Aleutians and Alaska.

In addition, our difficulties have been aggravated by the necessity of converting from natural to synthetic rubber in the manufacture of almost all rubber products. Natural rubber has been so satisfactory at low temperatures that, as a rule, very little consideration has been paid to the low temperature requirements of materials compounded from it, except in very few specific instances. Now the industry has suddenly been forced to become cold conscious, and the first thing that has occurred to everybody is that both natural and synthetic rubber to a greater or lesser extent at very low temperatures become brittle and break under sudden bending or shock. As a result, tests have been standardized on this basis, and these are the tests which have become common in the literature and upon which the performance of our natural and synthetic rubber compounds are judged. Such tests, while probably satisfactory for a piece of hose or some other item whose only mechanical service is occasional bending or flexing, are not at all adequate when we come to the subject of vibration insulators or such a specific branch as mountings for engines, machinery, and other purposes. The main function of such insulators or mountings is to reduce the transmission of vibration, and if they do not do this job, regardless of whether the mounting itself is easily destroyed by shock blow or not, they have lost all their ability to act as a vibration insulator and have, therefore, become valueless.

COMPOUNDS USED

In studying the effect of temperature, especially subnormal temperatures, on the vibration characteristics of various rubbers, the recipes which we have chosen for comparison were not selected on the basis of comparative test data, but were instead practical factory formulas made up for substitution purposes. Therefore the compounding of each recipe may differ considerably, since in each case factory processing and many other factors had to be considered

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besides the particular properties which are discussed in this paper. For that reason a number of inconsistencies are apparent in the data, and it should be realized that the properties of the various synthetics can be modified to a considerable extent by changes in compounding so as to accentuate any particular property. However the general conclusions drawn in connection with the main object of this paper, which is to demonstrate a new method of evaluating those properties of various elastomers that directly affect their ability to serve as vibration insulators, are to the best of our knowledge valid.

Some idea of the general quality of the stocks chosen for this work may be obtained from an examination of the physical test results given in Tables 1 and 2.

TABLE 1
PHYSICAL PROPERTIES OF 40-DUROMETER STOCKS

Stock	Tensile (lbs. per sq. in.)	Elongation (percent- age)	Modulus 300%	Compression set (B)	Torsional hysteresis (285° F)
Natural rubber	3230	750	180	13.6	0.047
GR-S	1550	700	360	25.0	0.102
GR-M	3000	970	280	30.0	0.076
GR-I	1850	700	600	17.6	0.091
Perbunan	1730	790	445	23.5	0.094

TABLE 2
PHYSICAL PROPERTIES OF 60-DUROMETER STOCKS

Stock	Tensile strength (lbs. per sq. in.)	Elongation (percent- age)	Modulus (300%)	Compression set (B)	Torsional hysteresis (285° F)
Natural rubber	3150	650	775	17.7	0.107
GR-S	1950	425	1415	18.9	0.077
GR-M	2150	630	880	40.0	0.118
GR-I	1700	430	1440	13.0	0.105
Perbunan	2000	460	1210	19.5	0.101

BRITTLE POINT VALUES

The conventional method of judging the above stocks for cold resistance resulted in the values listed in Table 3. The method of Selker, Winspear, and

TABLE 3
BELL TELEPHONE BRITTLE POINT

Stock	Brittle point (° F) (40-durometer stocks)	Brittle point (° F) (60-durometer stocks)
Natural rubber	-60	-60
GR-M	-37	-36
GR-S	-61	-61
GR-I	-51	-43
Perbunan	-6	-50

Kemp (*Ind. Eng. Chem.* 34, 137 (1942)) was used for these determinations.

It will be noted from this table of brittle point values that GR-S is fully equivalent to rubber, that GR-I is better than GR-M, and that both of these rubbers are satisfactory at temperatures below 30° F. Perbunan differs widely from the other rubbers, depending on the type of plasticizers used with it, and it should be noticed that the 60-durometer Perbunan stock, which contains a good freeze-resistant plasticizer, shows a brittle point of -50° F. It should

be remembered in this connection that brittle points can be varied considerably by compounding, but that they are also essentially affected by the polymer used.

STRESS-STRAIN CURVES AT VARIOUS TEMPERATURES

Our first attempt to obtain some insight into the properties of synthetic rubbers at various temperatures was to build a stress-strain tester with autographic features which could be easily used for the purpose of preparing stress term curves for any temperature. This machine was designed by E. F. Linhorst, and has a number of features which are of particular interest.

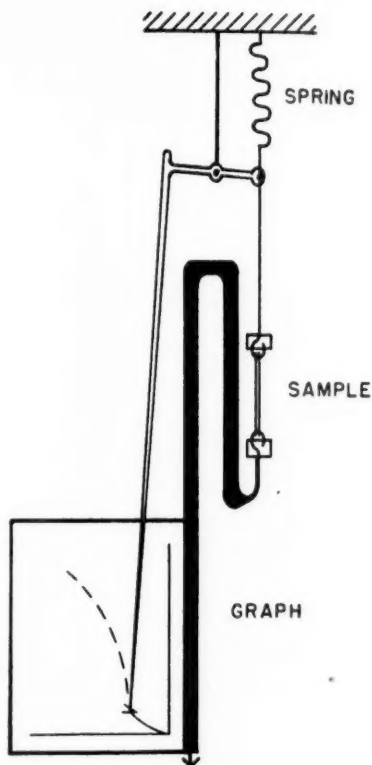


FIG. 1.—Diagram of recording stress-strain apparatus.

The machine is based on the principle of movement magnification with a lever of large arm ratio. As seen in the diagram (Figure 1), a T-50 test-piece one inch long is attached by one end to a rigid member carrying a chart, and as this is moved downward, the rubber is stretched. The other end of the rubber is attached to a stiff spring which has a deflection of 0.03-inch per pound of pull. This small deflection is magnified by a right-angle lever of arm ratio of about 32 to 1 and recorded horizontally with pen and ink. The graph has nearly rectangular coördinates, and one inch of movement of the pen horizontally represents about one pound of pull. The movement of the chart

is effected by a crank, cord, and pulley arrangement. Tests at lower temperatures can be made by immersing the sample into a Dewar flask containing alcohol cooled with dry ice. For higher temperatures hot ethyleneglycol can be used.

The machine pictured in Figure 2 was built of simple materials—wood and

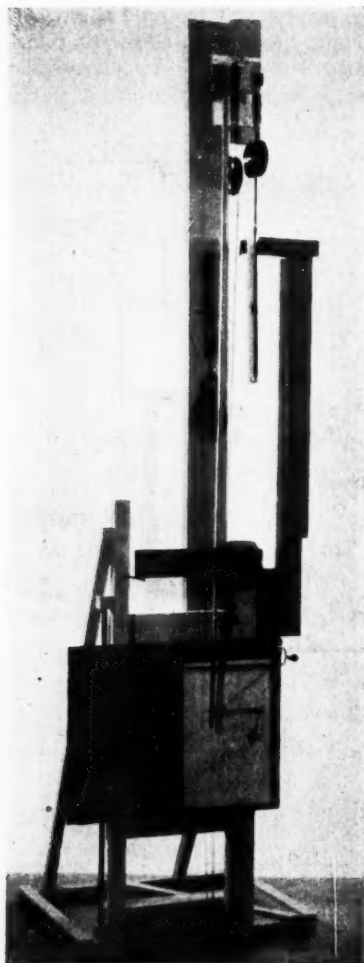


FIG. 2.—Recording stress-strain tensiometer.

few metal parts—and, while apparently crude in appearance, actually gives perfectly satisfactory readings within the experimental limit of accuracy. The most ingenious thing about this machine is the method of cooling or, if the occasion demands it, heating the samples. The whole arm holder test-piece can be inserted either in a Dewar flask for cooling, or in a flask with liquid kept at boiling temperature for heating. The simplicity of the attachment and the

ease with which it allows the use of a cooling solution of alcohol or dry ice have made it possible to obtain a great deal of interesting data.

The results obtained with this apparatus can be shown in a series of curves. For sake of simplicity, representative curves of 40-durometer natural and synthetic rubber stocks have been selected for discussion. Stress-strain curves at room temperature (Figure 3) of all the synthetics show a reasonable resemblance to natural rubber. At 0° F (Figure 4) the spread between the different

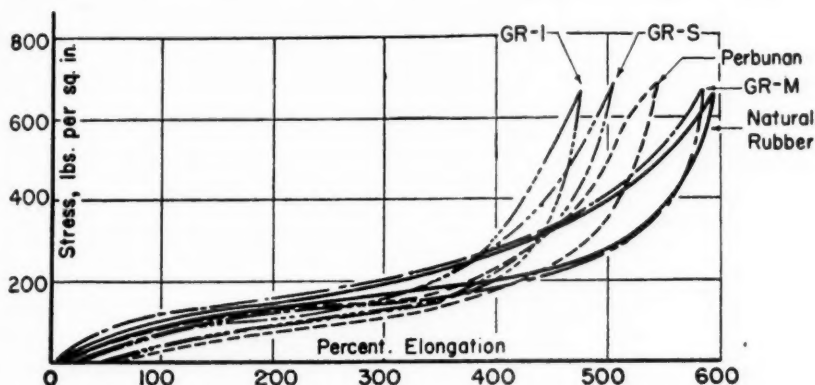


Fig. 3.—Stress-strain characteristics of 40-durometer stocks of various elastomers at room temperature.

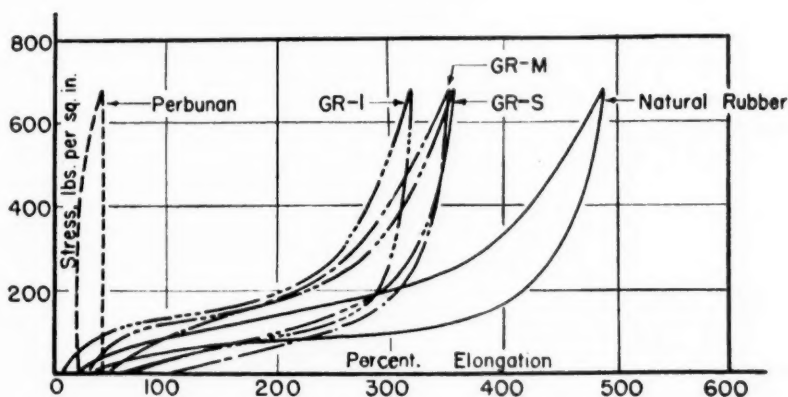


Fig. 4.—Stress-strain characteristics of 40-durometer stocks of various elastomers at 0° F.

synthetics has already become very marked. Natural rubber has been very little affected. GR-S and GR-M are still elastic; GR-I and Perbunan, which has not been compounded for cold resistance, are rapidly becoming stiff.

At -25° F (Figure 5) natural rubber is still elastic; GR-M and GR-S are showing a decided stiffening; GR-I is also stiff, and Perbunan has lost all flexibility. The temperature -40° F is the critical point referred to in most specifications. Natural rubber (Figure 6) is still elastic; GR-M has become very stiff along with Perbunan; while GR-S and GR-I are still slightly flexible. At -60° F (Figure 7) natural rubber has stiffened up to a very great degree,

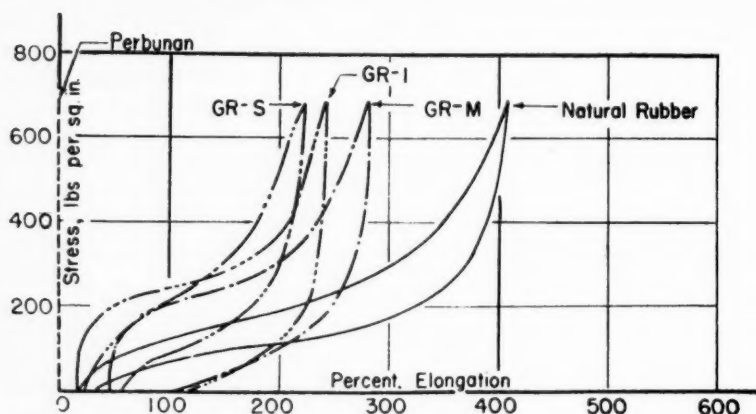


FIG. 5.—Stress-strain characteristics of 40-durometer stocks of various elastomers at -25°F .

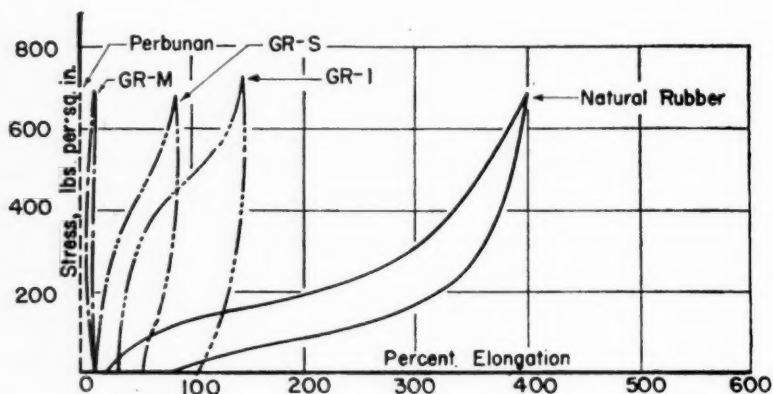


FIG. 6.—Stress-strain characteristics of 40-durometer stocks of various elastomers at -40°F .

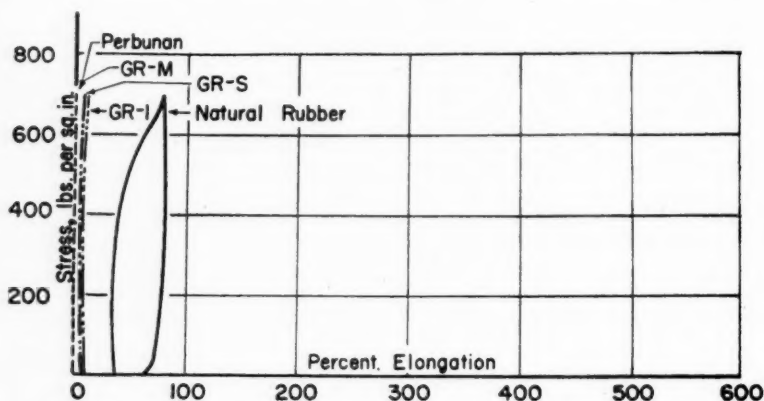


FIG. 7.—Stress-strain characteristics of 40-durometer stocks of various elastomers at -60°F .

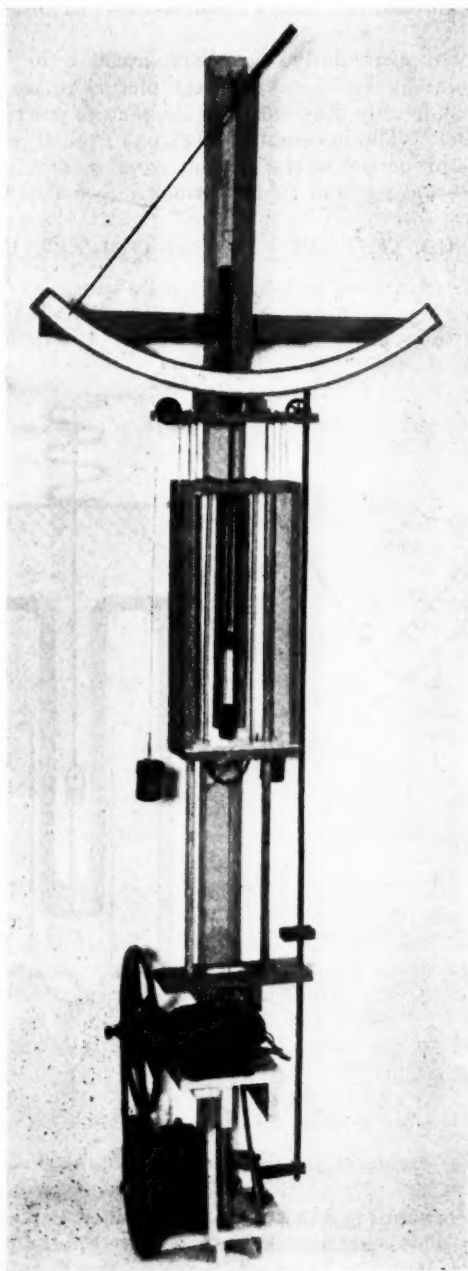


FIG. 8.—Machine to determine tensile strength over a range of temperatures.

but still retains some flexibility. All of the synthetics have become hard and lost all flexibility.

It should be noted particularly that a comparison of the stress-strain curves with the brittle point figures shows that the picture presented by the stress-strain curves is considerably different from the picture presented by the brittle point determinations. The information obtained from these curves serves as a warning that the properties of the synthetics vary much more widely under changing temperature conditions than previous data had revealed.

TENSILE TESTS AT VARYING TEMPERATURES

Some other data of interest may be the tensile strength of various synthetic rubbers at different temperatures, and for this we have again built a tensile

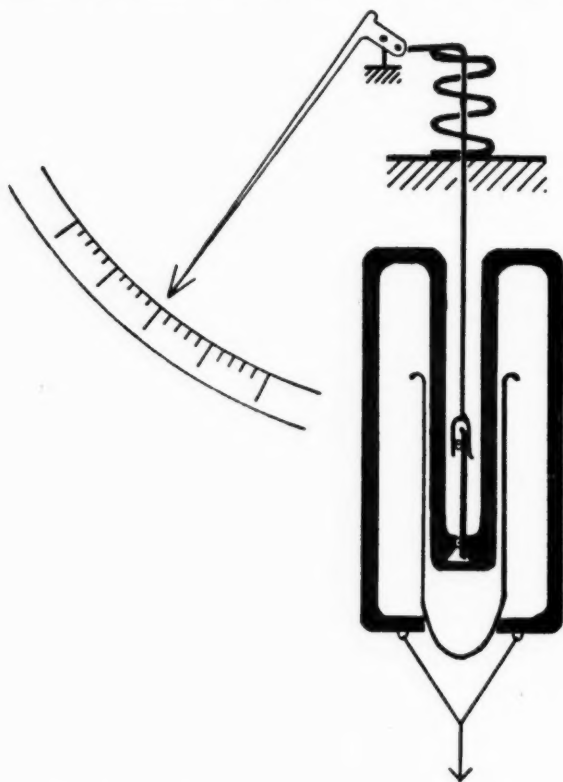


FIG. 9.—Diagram of variable temperature tensile strength tester.

testing machine incorporating a test-piece holder which can easily be immersed into a glass flask. This machine, shown in Figure 8, obtains tensile strength values in a manner similar to the Scott machine, but is so designed that the tests may be made at different temperatures. As may be seen from the diagram (Figure 9), one end of the usual dumbbell test-piece is attached to a force measuring device, while the other end is stretched by a motor and speed

reducing mechanism at a rate of 20 inches per minute. For temperatures down to -50°C , the sample is immersed into a large test-tube 17 inches long, filled with alcohol and cooled with dry ice. The test-tube can be insulated with cellophane. For temperatures below -50°C , a Dewar flask can be used. For testing at high temperatures, the test tube is filled with heated ethylene-glycol. The force measuring device is similar to that of the tensiometer, but is not self-recording.

The tensile strength of natural and the various synthetic rubbers over a range of temperatures from $+260^{\circ}\text{F}$ to -60°F is shown in Figure 10. As

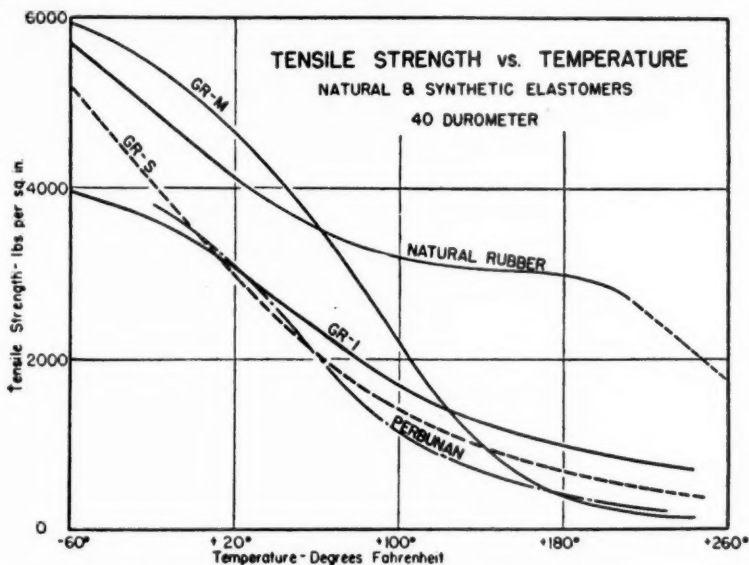


FIG. 10.—Tensile strengths at different temperatures of 40-durometer stocks of various elastomers.

may be seen from these curves, natural rubber is much stronger at elevated temperatures than any of the synthetics, and it is only surpassed at lower temperatures by GR-M. At the higher temperatures GR-M has the least strength of all the rubbers, but at about room temperature it becomes equal to natural rubber, which is in accordance with general observations. Other synthetics are lower than natural rubber, with GR-I the best at high temperatures and with GR-S following the natural rubber curve quite closely, although lower at all points.

MEASUREMENT OF VIBRATION TRANSMISSION

While all of these data are of considerable interest, however, we still did not have any direct positive evidence of the actual effect of different synthetics at varying temperatures on the transmission of vibration. Mr. Linhorst again designed and built what we call a sheer resiliometer, by which it is possible actually to measure the amount of vibration transmitted through a mounting under varying temperature conditions by measuring the applied amplitude of vibration compared with the transmitted amplitude of vibration. This device simulates the conditions that exist when a delicate instrument such as a radio

is attached to the vibrating frame of an airplane or motor car by means of rubber mountings. This machine is illustrated in Figure 11, and a diagram showing the principles involved in its operation is found in Figure 12.

One side of the mounting is forcibly vibrated by a constant speed (1800 r.p.m.) motor, with an eccentric pin on the end of the shaft. The other side

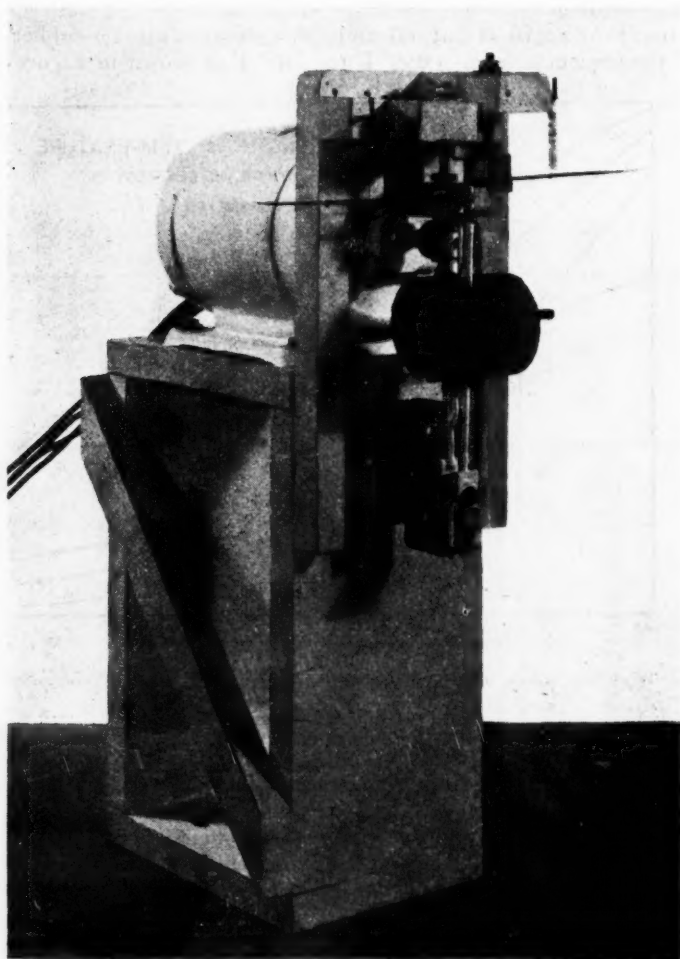


FIG. 11.—The shear resiliometer.

of the mounting carrying the load receives whatever fraction of the applied vibration is transmitted by the mounting. The amplitudes of the vibrations, 0.015-inch or less, are too small to be seen directly, and they are therefore magnified ten times by a light weight lever six inches long made of thin metal of right angular cross-section. The ratio between the transmitted and applied amplitudes is called the vibrational transmissibility. Tests can be made at

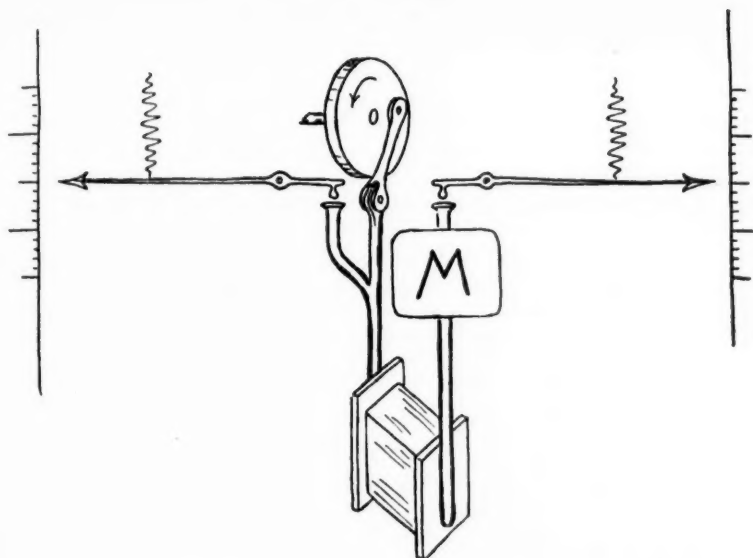


FIG. 12.—Schematic drawing of shear resiliometer.

temperatures either above or below that of the room by the use of alcohol cooled with dry ice or heated glycol.

With this instrument it was possible to determine the amount of vibration transmitted over a range of temperatures, and from the results obtained, to prepare a comparative chart showing the relative efficiency of the different synthetics and natural rubber at various temperatures. The variation with temperature of the vibration transmitted by the different rubbers as 40-durometer stocks, expressed as "percentage transmission" is given in Figure 13.

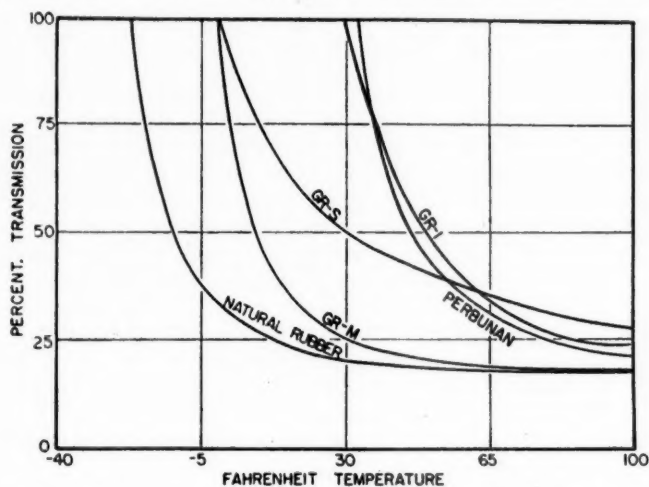


FIG. 13.—Percentage transmission of vibration of 40-durometer stocks of various elastomers at different temperatures.

Natural rubber and GR-M are practically equivalent at room temperature; while at 10° F natural rubber is still as good as GR-M at 30° F. At -5° F, natural rubber, although it has started to lose its ability to absorb vibration, still has some merit; while GR-M has completely lost any ability to absorb vibration. GR-S at room temperature is not so good as natural rubber, but as the temperature drops, it does not lose its ability to absorb vibration so rapidly as GR-M. Both GR-M and GR-S ultimately are definitely inferior to natural rubber. GR-I and Perbunan, if the latter has not been compounded for freeze resistance, show a rapid loss of their ability to absorb vibration because of their characteristics of stiffening quickly with comparatively small reductions of temperature below 75° F.

With the 60-durometer stocks the picture, as shown in Figure 14, is nearly the same, except that, with the higher durometer stock to start with, slightly

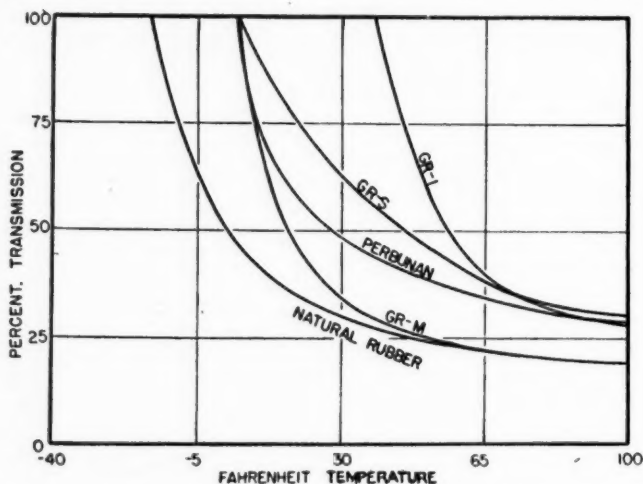


Fig. 14.—Percentage transmission of vibration of 60-durometer stocks of various elastomers at different temperatures.

less resistance to cooling is shown. The natural rubber stocks still show great superiority. One interesting difference is that the 60-durometer Perbunan stock now shows relatively better ability to absorb vibration, which can be explained by the fact that this stock was specially compounded with freeze-resisting plasticizer.

Effect of initial deflection on vibration transmission.—It should be kept in mind that the amount of vibration transmitted by any particular stock depends not only on the stock being used, and the temperature at which it is being tested, but also on the initial deflection of the sample. The importance of this can well be illustrated by Figure 15, which shows the variation in percentage vibration transmission depending on the initial deflection. It will be noted that, as the loading is increased, the performance is improved. From this point can be drawn the conclusion that if the bond and elastomer are sufficient to resist greater strain, then the designs which have high initial deflection will be the most successful at low temperatures.

Barrier points of various rubbers.—It is a common belief among many people that the problem of freeze resistance in mountings is not too serious because

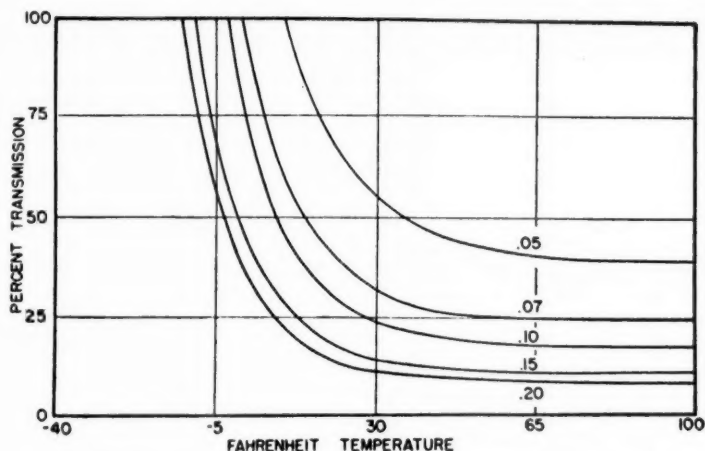


Fig. 15.—Effect of varied load deflection on percentage transmission of vibration for 40-durometer GR-M stock.

the mountings warm up when they are vibrated. We have found, however, that in any given system there is a definite temperature below which a mounting does not warm up, no matter how long it is vibrated. This temperature depends on a number of factors: the stock itself, the shape of the mounting, the initial deflection, the radiation and conduction permissible in the system, and the frequency and amplitude of the vibration. We call this critical temperature the *barrier point*, and Figure 16 illustrates barrier points for the shear resiliometer system itself, using 40-durometer stocks of various elastomers in

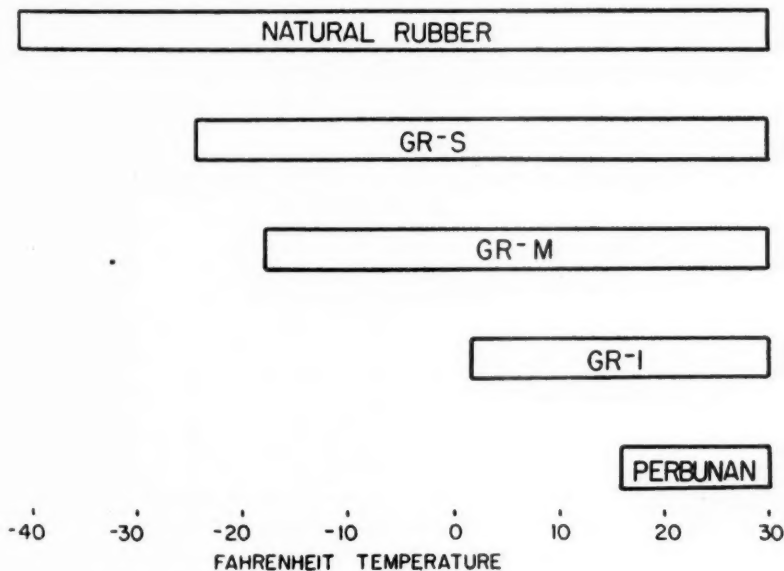


Fig. 16.—Barrier point values of various elastomers in the shear resiliometer.

dry ice and alcohol mixtures. Note that natural rubber under such conditions warms up at temperatures just above -40°F . Other elastomers, as shown, have higher barrier points and thus will become ineffective at much warmer temperatures than natural rubber. Unquestionably this ability of the mounting to warm up when vibrated is an extremely important factor in making mountings that will be practically serviceable at temperatures where static tests would indicate complete failure.

SUMMARY AND CONCLUSIONS

The results of this work have been to show that the effect of temperature on the functions of vibration insulators is much greater than would be supposed from the type of tests which have become more or less common in the industry for determining the effect of low temperatures on various elastomers. It has shown also that natural rubber is the outstanding material for vibration insulation at subnormal temperatures. The substitution of any of the synthetics for natural rubber is a problem which requires not only a thorough study of compounding, but also of the practical conditions under which the particular mounting or insulator is supposed to function. An improvement in vibration insulation over a wide range of temperatures may be obtained by means of increased initial deflection. A critical point, called the "barrier point", which depends not only on the compound but on the design and application of the mounting, is defined.

New laboratory methods have been devised to obtain information which design engineers can apply to practical problems. This equipment actually shows the percentage of transmission of vibration. New equipment for the determination of stress-strain curves and tensile tests at all temperatures are likewise described and their uses explained.

We hope that the simple, yet accurate instruments which have been devised from commonly available materials will be of some encouragement to others who wish to investigate the properties of different elastomers over a range of temperatures, but are hampered by the limitations of priorities, expense, and the fact that there is a lack of suitable equipment on the market for such investigations.

DEFORMATION OF RUBBERLIKE MATERIALS *

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In a recent paper on the highly elastic deformation of polymers, Aleksandrov and Lazurkin¹ give the following expressions, first for the total deformation $D(t)$ of rubber at time t after application of a constant stress:

$$D(t) = D_0 + D_\infty (1 - e^{-t/\tau}), \quad (1)$$

and second, for the amplitude D of deformation under a harmonic stress:

$$D = D_0 + \frac{D_\infty}{1 + i\omega\tau}; \quad (2)$$

where D_0 is the "ordinary elastic" component, which is very small compared to D_∞ ; D_∞ the "highly elastic" component, obtained for $t \rightarrow \infty$ in (1) or $\omega \rightarrow 0$ in (2); ω is $2\pi \times$ the frequency of the applied stress; τ a "relaxation time".

It may be noticed that Expressions (1) and (2) would be given by the mechanical model shown in Figure 1, where K_0 is the stiffness of a spring

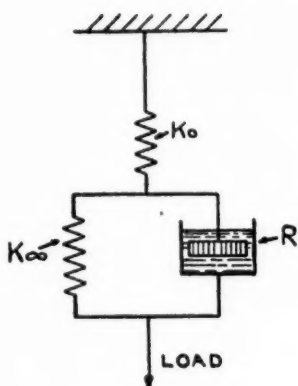


FIG. 1

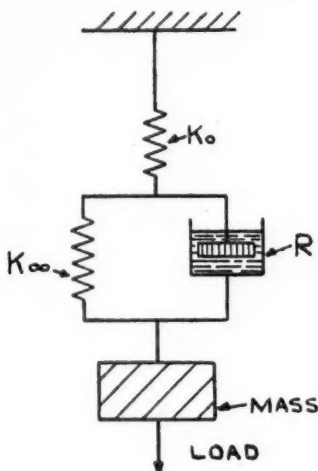


FIG. 2

corresponding to the "ordinary (crystal) elasticity"; K_∞ one corresponding to the "high elasticity"; R the "damping coefficient" of a dashpot in parallel with the spring, giving rise to a viscous force proportional to the velocity. When a constant force F is applied to the system, the solution of the equation

* Reprinted from *Nature*, Vol. 153, No. 3895, pages 777-778, June 24, 1944.

of motion gives the displacement:

$$D(t) = \frac{F}{K_0} + \frac{F}{K_\infty} (1 - e^{-tK_\infty/R});$$

while for a harmonically varying force $Fe^{i\omega t}$ the steady state solution is a harmonic displacement of frequency $\omega/2\pi$ and amplitude D :

$$D = \frac{F}{K_0} + \frac{F}{K_\infty + i\omega R}. \quad (4)$$

(3) and (4) reduce respectively to (1) and (2) on writing $D_0 = F/K_0$; $D_\infty = F/K_\infty$; $\tau = R/K_\infty$.

If one considers a rubber unit stressed, for example, in shear, it is easy to see that on introducing an elastic modulus G and a "normal viscosity coefficient" ν (cf. Kimball²) the "relaxation time" τ has the expression:

$$\tau = R/K_\infty = \nu/G. \quad (5)$$

It is of interest to compare the results of Aleksandrov and Lazurkin¹ with those of other workers using the free or forced vibrations of tuned systems, as shown in the mechanical model of Figure 2. The "ordinary" elasticity was neglected by these authors ($1/K_0 = 0$); a justifiable approximation for the type of polymers and range of temperatures in their work.

An advantage of the tuned-system method is that it permits the separate determination of elastic and viscous forces. The elastic modulus is determined from the frequency of the free vibration³, or from the frequency of resonance of the forced vibration⁴. The viscosity coefficient is determined from the rate of decay of the free vibration³, or from the amplitude at resonance of the forced⁴. The "relaxation time" is then determined from Equation 5: $\tau = \nu/G$. Now, all the authors quoted⁵ have found that G varies little, if at all, with frequency, while ν is roughly inversely proportional to frequency. This fits in better with the phenomena of elastic hysteresis connected with ordinary elastic solids² than with the notion of a "relaxation time" constant at a given temperature. To connect these results with the "freezing" of rubber with increased frequency observed by Aleksandrov and Lazurkin¹, one would expect the curve of τ vs. frequency to start at low frequencies roughly in the shape of a rectangular hyperbola, but tend asymptotically with increasing frequency to a constant positive value. The determination of G and ν over a wide range of frequencies and temperatures would not only be of theoretical interest, but also of great practical value in the engineering application of rubber. One further point that is best brought out by the forced vibration method is the departure from linearity of elastic and viscous effects in rubber: it is found that the measured values of G and ν vary with the amplitude of strain.

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STIFFENING EFFECT OF PIGMENTS IN RUBBER *

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The use of reinforcing pigments in rubber, especially in synthetic rubber, is important in securing desirable physical properties. The earlier literature on the subject has been reviewed by Shepard, Street, and Park¹. Several theories were advanced to explain the effectiveness of reinforcing pigments in rubber. Some of these emphasized the importance of particle size and shape; others, the chemical composition and surface activity. The electron microscope has now furnished more reliable information on the particle size and shape of pigments, especially of carbon blacks, than was available in the earlier work². The carbon blacks used in rubber compounding are essentially spherical; the mean diameter varies from 28 to 274 m μ for different types. Systematic studies have been carried out to show the influence of particle size and surface area on various physical testing indices used to evaluate rubber compounds³. The x-ray structure of rubber stocks containing carbon black has been investigated⁴. Several articles dealing with the theory of pigment reinforcement have appeared⁵.

This additional work has not clarified the original concepts advanced to explain filler reinforcement, but the research of Wiegand shows beyond doubt that particle size is the predominating factor in explaining differences in the properties of rubber compounded with various blacks. The present paper will attempt to explain some of the effects of pigment reinforcement of rubber, particularly increased stiffness, by simple mechanical considerations which may be regarded as extensions or extrapolations of the results of measurements on rubber in compression.

EFFECT OF SHAPE ON STIFFNESS OF COMPRESSED RUBBER

The analysis of what happens when a piece of rubber is compressed between parallel plates has disclosed a complicated set of circumstances. Because of the practical interest in such deformations of rubber, the work has been thorough⁶ and the principles are well understood. It has been found that, if the bearing surfaces are lubricated, the compression modulus is independent of the shape of the test-piece, and is characteristic of the rubber compound. If the rubber is attached by vulcanization to the surfaces or is prevented by friction from slipping at the surfaces, the situation is different, and the apparent modulus depends on the shape of the test-piece, particularly on the ratio of load area to free area. When there is no slipping at the surfaces, the stress distribution is complicated. Not even the pressure on the loading plates is uniform but diminishes toward the edges.

As the load-bearing area is increased relative to the free area, the restraint at the surface becomes increasingly effective in raising the apparent modulus

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or stiffness of the rubber. It has been found empirically that the ratio, load area/free area, which is called "shape factor", can be employed, by the use of appropriate curves, to estimate the stiffness for a wide range of shapes and sizes of rubber pieces for compressive deformations. Figure 1 shows two such

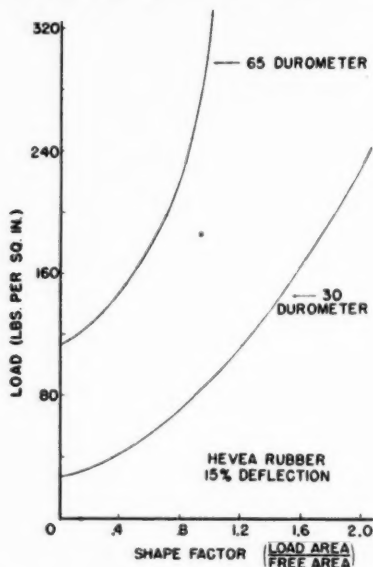


FIG. 1.—Shape factor curves (data of Kimmich⁷).

curves reproduced from data published by Kimmich⁷. Test-pieces of similar shape but varying in size undergo the same percentage deformation with the same applied compressive stress.

The principle of the increase in compression stiffness by the use of restraining surfaces is illustrated, in Figure 2, by the effect of passing parallel septa

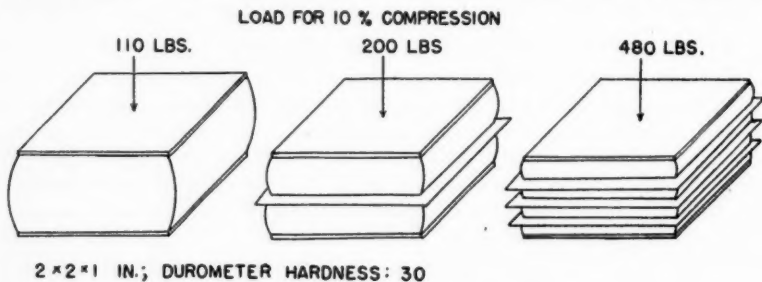


FIG. 2.—Effect of restraining surfaces on stiffness.

through a block of rubber. If the septa and end-plates are lubricated, the stiffness is unaffected by the number and position of the septa. When the rubber is adhered to the end-plates and septa as shown, a large increase in stiffness occurs. Incidentally, it can readily be proved that the stiffness of such a system, for a given number of septa, is a maximum when the septa are

uniformly spaced. In the picture which will be developed, the pigment particles will be considered to provide the restraining surfaces. If the simple model of Figure 2 can be used, it follows that a uniform pigment dispersion should give maximum stiffness.

Since the use of a shape factor rests entirely on empirical considerations, it is to be expected that there will be limitations on its range of applicability. Hirshfeld and Piron⁸ observed that a square test-piece, $\frac{1}{8}$ inch thick, was appreciably stiffer than a long, narrow piece with the same shape factor but twice the thickness. Kimmich confirmed this; his curves are reproduced in Figure 3. Thus there may be a limit to the range of the absolute thickness

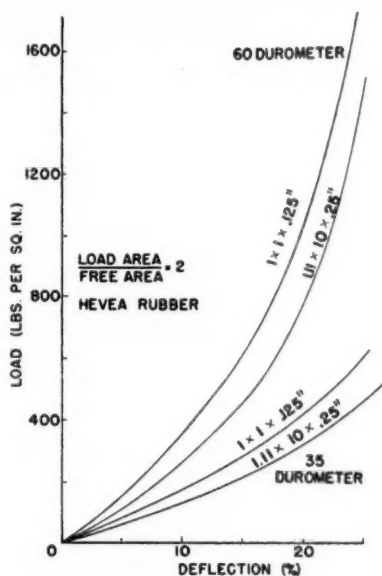


Fig. 3.—Effect of thin test pieces⁷.

for which a shape factor, based on relative areas alone, can be consistently used. This does not necessarily mean that the idea of a useful shape factor no longer applies for thin pieces. It is more reasonable to suppose that curves which will be like those shown in Figure 1, but displaced to higher stresses, will apply in a range of smaller absolute thicknesses. At any rate, this will be assumed for the purposes of this theory of pigment reinforcement. More experimental data, especially for very thin pieces of similar shape, would be desirable.

THEORY OF PIGMENT REINFORCEMENT

An effort will be made to extend the relations discussed in the previous section to explain some of the effects of pigment reinforcement of rubber. In many respects the rubber in a loaded stock subjected to compression can be regarded as working under conditions analogous to those obtaining for a gum stock when the shape factor is relatively high. Rubber films exist between pigment particles to which they are firmly attached. For ordinary volume loadings, the thickness of these films is of the same order of magnitude as the

particle diameter. x-Ray patterns indicate that there is a complicated stress distribution in a loaded stock which also exists for a gum stock with high shape factor. The conditions when a film of rubber in a loaded stock is compressed between pigment particles do not correspond closely with the experimental conditions for which the shape factor relations were found. For spherical particles of carbon black, the loading surfaces are not flat and, strictly speaking, there is no free surface for the compressed films. Nevertheless, under compression the rubber in the thinner portions of the compressed films undoubtedly tends to move out into the adjacent regions where the rubber is thicker. The concept that the rubber in a loaded stock is working at a higher shape factor seems to account in a qualitative way for the general behavior of loaded stocks in compression, as will be shown in this article.

EFFECT OF VOLUME LOADINGS AND PARTICLE SIZE ON STIFFNESS

To secure some idea of the thickness of the rubber films between particles for various volume loadings of carbon black, it is advantageous to use the results derived from the packing of spheres⁹. There are two extreme types of packing for spheres, rhombohedral or "closest" packing and cubical or "most open" packing (Figure 4). In a rubber stock containing carbon black, an

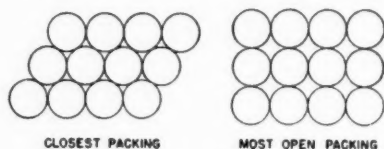


Fig. 4.—Two-dimensional illustration of types of packing.

idealized structure can be imagined in which the particles are surrounded by spherical shells of rubber. These shells are thought of as packing according to one of the schemes in Figure 4. The interstices or pores are then to be regarded as filled with rubber (Figure 5). It should be emphasized that no physical distinction or boundaries are implied between the rubber surrounding the particles and the rubber in the pores. The picture is merely an aid to thinking and a help in applying the calculations from the packing of spheres. The following notation will be used:

V = volume of pigment in 100 volumes of rubber

d = mean particle diameter

D = diameter of imaginary rubber shells around particles

p = porosity of packing of rubber shells = ratio of volume of imaginary pores/total volume

The number of pigment particles in a compound containing 100 volumes of rubber and V volumes of pigment will be $6V/\pi d^3$ (that is, V divided by the volume of a single particle). The total volume, $100 + V$, corrected for the imaginary porosity by multiplication by the factor $(1 - p)$ will equal the volume of the pigment rubber spheres. Since there are $(6V/\pi d^3)$ of these spheres, their total volume is $(6V/\pi d^3)$ multiplied by $(\pi D^3/6)$. Expressing these relations in the form of an equation:

$$(100 + V)(1 - p) = V D^3/d^3 \quad (1)$$

For closest packing, $p = 0.26$ (from geometry); for most open packing, $p = 0.48$. Actually, p will probably have some intermediate value.

The average minimum thickness of the rubber films between particles will be $D - d$. From Equation 1:

$$D - d = \left[\sqrt[3]{\frac{100 + V}{V}} (1 - p) - 1 \right] d \quad (2)$$

This shows that the thickness of the rubber film between particles for any given volume loading is proportional to the particle diameter. If the type of packing does not change, the structure in the stock for large particles is simply a magnification of the structure for small particles. It follows from the principle of similarity (rubber test-pieces of similar shape undergo the same percentage deformation under the same compressive stress) that the stiffness of the films should depend on the volume loading but not on the particle size.

The stress for 300 per cent elongation, commonly called the 300 per cent modulus, is, in fact, insensitive to particle size. As a result of his survey of carbon blacks varying in average diameter from 274 to 13 μ Wiegand¹⁰ con-

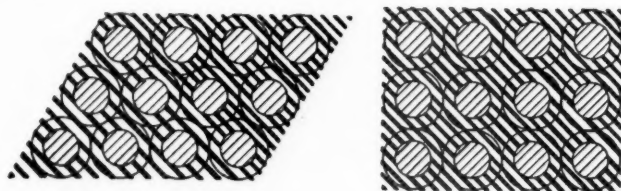


FIG. 5.—Representation of pigment dispersion in rubber.

cluded that "modulus (at 300 per cent) presents little discernible response to increasing surface", *i.e.*, particle size. Shore hardness was more dependent on particle size. For GR-S there is a secondary upward trend in both modulus and hardness with surface¹¹. There is a definite dependence of the compression modulus on the particle size for a given volume loading. This is shown by the curves in Figure 6. According to the theory here proposed, this is a second-order effect due to a dependence of the stiffness of the films, not only on shape factor but on the absolute thickness as illustrated for large test-pieces by the curves of Figure 3. Since, as already shown, the thickness of the rubber between particles is proportional to the particle diameter, there is approximately a tenfold variation in film thickness for stocks containing the same volume loadings of Wyex and Thermatomic blacks¹². The data plotted in Figure 6 indicate a stiffness ratio for stocks with the two blacks of 1.56 at 10-volume loading and 2.14 at 30-volume loading. The variation in stiffness is small compared to the variation in particle size. The fact that the stiffness ratio for the two blacks increases with volume loading, *i.e.*, as the film thickness becomes smaller, tends to confirm the supposition that the effect is due to a dependence of stiffness not only on the shape factor but also on the absolute value of the film thickness.

Equation 2 can be used to compute the thickness of the rubber films between particles as a function of the volume loading. Results of such calculations are shown in Table I. An ideal dispersion is assumed. For an actual

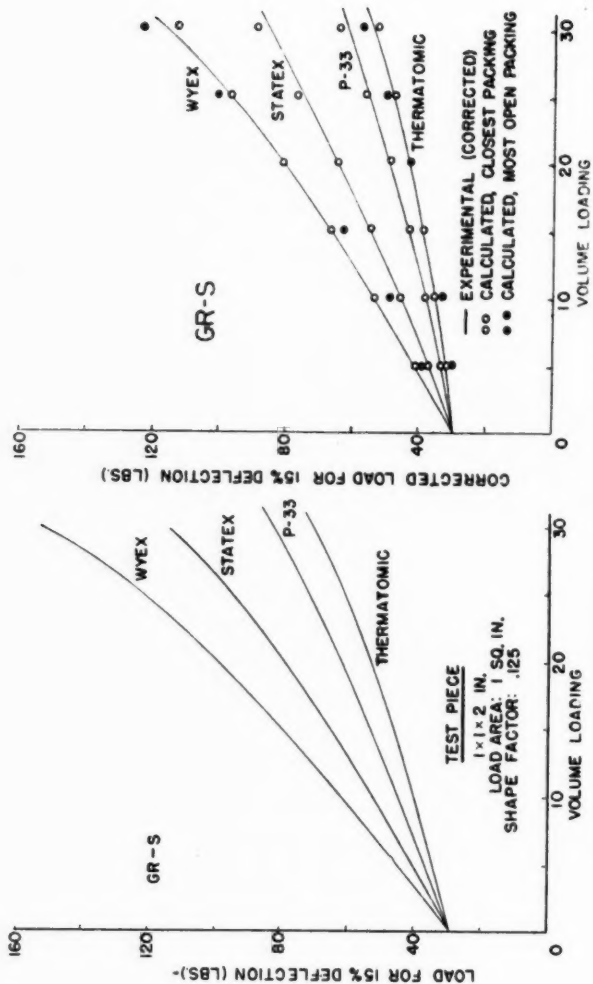


Fig. 6.—Load-compression curves.

Fig. 7.—Comparison of theory with experiment.

TABLE I
THICKNESS OF RUBBER FILMS BETWEEN PARTICLES

V	Closest packing		Most open packing	
	$\frac{D}{d}$	Film thickness, $D - d$	$\frac{D}{d}$	Film thickness, $D - d$
5	2.50	1.50 <i>d</i>	2.22	1.22 <i>d</i>
10	2.01	1.01 <i>d</i>	1.79	0.79 <i>d</i>
15	1.78	0.78 <i>d</i>	1.59	0.59 <i>d</i>
20	1.65	0.64 <i>d</i>	1.46	0.46 <i>d</i>
25	1.55	0.55 <i>d</i>	1.37	0.37 <i>d</i>
30	1.48	0.48 <i>d</i>	1.31	0.31 <i>d</i>

dispersion, which may depart from the ideal rather widely, the results may be considered to represent average values.

Actually, taking into consideration the particle size distribution, the packing is probably quite heterogeneous. The assumption of any systematic packing can be justified only by considering that it may give an average result. The results in Table I taken in conjunction with the shape factor curve for 30-durometer stock (gum stock) in Figure 1 can be used to predict the course of the curves for compression load *vs.* volume loading.

These curves (Figure 6) should first be corrected for the volume of black present. Some of the stiffness of a loaded stock is due merely to the fact that a certain volume of rubber has been replaced by pigment. Since practically all the strain takes place in the rubber, a given percentage strain of the compound implies a larger strain of the rubber in the compound. The correction factor, as pointed out by Morrison⁴, is $100/(100 + V)$. If the compression loads for the same deflection are multiplied by this factor, they will all be on a comparable basis in regard to this volume effect. At the highest loading used (30 volumes) the correction amounts to 23 per cent. This is the increase in stiffness to be expected because some of the rubber has been replaced by black. After being corrected in this way, the curves of Figure 6 are replotted in Figure 7.

To test the theory, it can be assumed that the effective shape factor for the rubber films between particles at different volume loadings of the same black is inversely proportional to the thickness of the film. A definite example will be cited to illustrate the procedure: The compression load at 15 per cent deflection for the 20-volume Wyex loading (Figure 7) is increased in the ratio, $81/30 = 2.70$, over that for no loading. From the shape factor curve for the gum stock in Figure 1, an increase in the load in this ratio implies that the shape factor is 0.83. If the shape factor for the rubber films for the 20-volume loading of Wyex is taken as 0.83, values for the shape factor for other loadings can be calculated as being inversely proportional to the film thicknesses in Table I. This leads to the values in the second column of the following table:

Volume loading	Calculated internal shape factor (closest packing)	Load (15% deflection) (lbs. per sq. in.)	
		From curve of Figure 1	Adjusted to actual load for $V = 20$
5	0.36	38	41
10	0.53	49	53
15	0.68	61	66
20	0.83	74	80
25	0.98	90	97
30	1.13	106	114

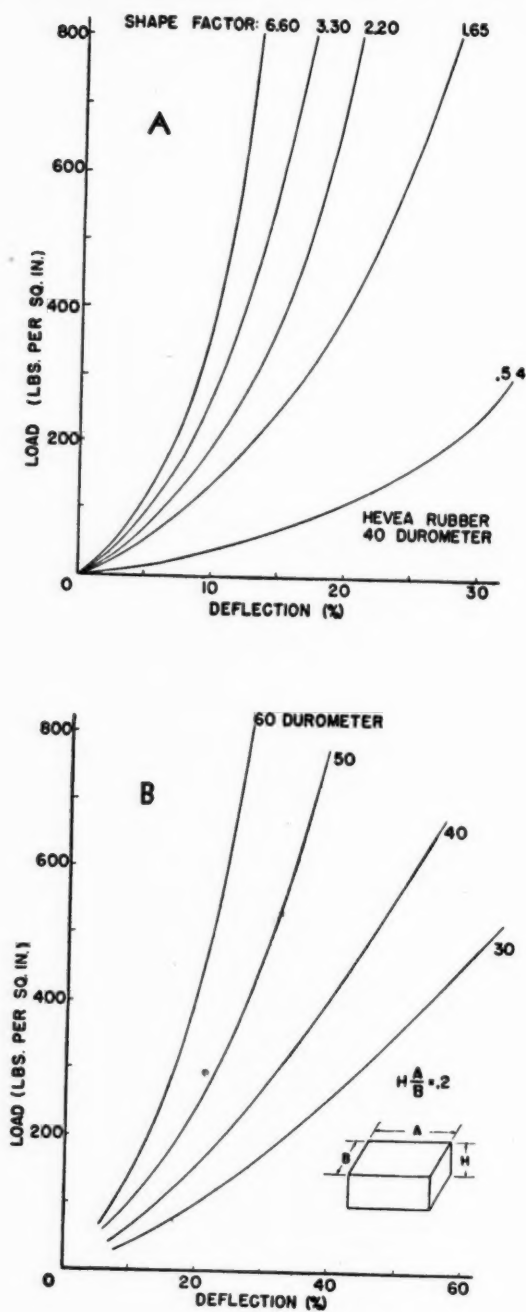


Fig. 8.—Legend at bottom of cut on next page.

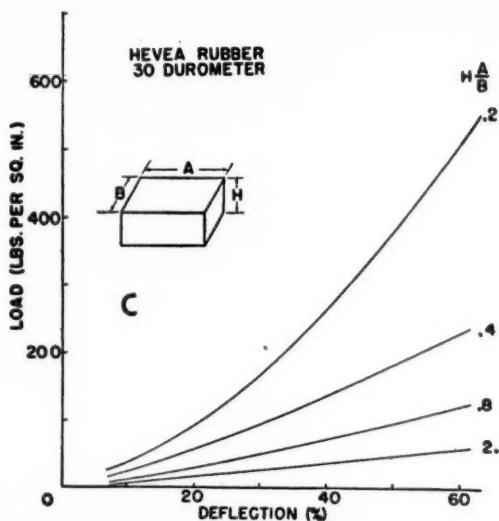


Fig. 8.—Effect of shape factor (A), of durometer hardness (B), and of shape (C) on load-deflection curves¹².

The third column shows the loads, from Figure 1, corresponding to the shape factors in the second column. In the fourth column these loads have been multiplied by a small correction so that the load predicted for the 20-volume loading will fit the experimental curve of Figure 7. Figure 7 shows that the calculated points for closest packing coincide with the experimental curves. When the calculations are made on the basis of the most open type of packing, there is some deviation of the calculated from the experimental values.

No great exactness can be claimed for the above procedure since the shape factor curve of Figure 1 cannot be expected to apply exactly for the thin films in a loaded stock. The agreement found does lend plausibility to the view that a similar type of curve explains the dependence of stiffness on volume loading.

SHAPE OF LOAD-COMPRESSION CURVES

Some of the general characteristics of the load-compression curves for loaded stocks can be interpreted as shape factor effects. The curves in Figure 8A, taken from a paper by Smith¹³, illustrate the fact that, as the shape factor is progressively raised, the curvature near the origin increases. The curves in Figure 3 show the same sort of increased curvature for the 60-durometer stock compared to the 35-durometer stock. In terms of the theory here proposed, this increased curvature is attributed to the fact that the rubber films between the pigment particles in the 60-durometer stock have a higher shape factor than in the 35-durometer stock because they are thinner.

The curves in Figure 8B¹³ show the effect of durometer hardness, which is controlled by pigment loading, on the shape of the load-compression curves. The curves in Figure 8C, for comparison, show the effect of increasing the shape factor for a 30-durometer stock where the pigment loading is small or negligible. The similarity in the two families of curves in B and C is submitted as evidence that the shape factor of the rubber films between particles in

loaded stocks is a predominating factor in accounting for the effects of pigment loading on load-deflection curves. The difference in the shape of the two curves in Figure 1 is also amenable to this type of explanation.

DYNAMIC AND STATIC MODULUS

An examination of the relations existing between shape factor, durometer hardness, and static and dynamic compression stiffness discloses further reasons for believing that internal shape-factor effects occur in pigmented stocks. Figure 9 shows the divergence between the static and dynamic

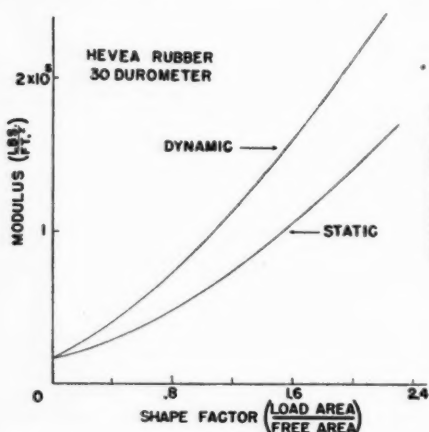


FIG. 9.—Effect of shape factor on static and dynamic tests.

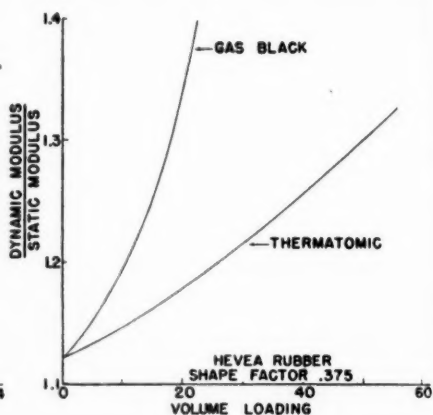


FIG. 10.—Effect of pigment loading on static and dynamic tests.

compression moduli at higher shape factors for a gum stock of 30 durometer hardness¹⁵.

In Figure 10 the ratio of dynamic to static modulus is plotted as a function of volume loading for gas black and Thermatonic loadings. The ratio of dynamic to static modulus increases with pigment loading, which would be predicted if this divergence were a shape-factor effect dependent on the effective shape factor of the rubber films between pigment particles.

LIMITATIONS OF THEORY

The explanations offered for some of the effects of pigment loadings in rubber appear adequate for the range of phenomena considered, and are so plausible that they should probably be taken into account in the explanation of all reinforcement phenomena. Many important aspects of pigment reinforcement, such as the effect on resilience, have not been touched on, since no data were available on the resilience of thin films in compression. Experimental work on that point might well be successful in extending the theory. Undoubtedly there are many aspects of reinforcement which are not controlled by the relatively simple mechanical ideas advanced here to explain compression stiffness. Variations from results to be expected on the basis of a straight-forward shape factor interpretation might occur for a number of reasons. Among these should be mentioned particle size distribution, particle shape,

and especially pigment dispersion. Still the idea should persist that the effects are largely mechanical in a more complicated system. It should be pointed out that there is, in some cases, a variation in the stiffening effect of pigment loadings for different types of rubber. Thus pigment loadings are relatively ineffective in stiffening Butyl rubber¹⁶. This may be related to the type of dispersion secured. At any rate, curves of the effect of shape factor on the stiffness of Butyl-rubber gum stock would have to be studied before this fact could be advanced as an argument against the theory. One of the most important consequences of the theory should be to emphasize the importance of pigment dispersion.

ACKNOWLEDGMENT

The data for Figure 6 were kindly furnished by L. H. Bennett of the Synthetic Compounding Section.

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VULCANIZATION OF BUNA-S (GR-S) WITH ORGANIC SULFUR COMPOUNDS.

II.

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INTRODUCTION

In a previous paper¹, extensive data were shown on vulcanizates of Buna-S (GR-S) in which alkylxanthogen sulfides were used as vulcanizing agents. These data showed conclusively that marked improvement in physical properties, resistance to heat embrittlement, resistance to flex-cracking and heat generation were obtained by the use of this type of vulcanizing agent. This paper presents results obtained in the vulcanization of Buna-S (GR-S) with other types of organic sulfides, a few of which were briefly mentioned in the previous paper.

EXPERIMENTAL PROCEDURE

The procedure used in these studies was the same as described in the previous paper.

DISCUSSION

The organic sulfides prepared and used in these vulcanization studies have been arranged in eight groups, and the properties of the vulcanizates are described briefly. These are shown in Table I. The base formula used for all groups of compounds is shown in Table II.

GROUP I—*Aliphatic sulfides*.—None of the compounds shown in Table III exhibited any vulcanizing activity.

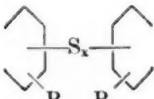
GROUP II—*Aromatic sulfides*.—None of the compounds shown in Table IV exhibited any vulcanizing activity.

GROUP III—*Miscellaneous sulfides*.—Of the compounds shown in Figure 1, only No. 7, the disulfide from pinenethiol, showed any vulcanizing activity. It is of interest to note that Compound No. 6, pinene tetrasulfide, exhibited no vulcanization characteristics, whereas No. 7, in which the pinene had reacted with hydrogen sulfide and had formed a disulfide, yielded a vulcanizate of fair properties, although heat generation was high.

GROUP IV—*Acid sulfides*.—The percentage used, accelerator, and conditions shown in Figure 2 and in subsequent figures represent the best all-round properties that were obtained. It is of interest to note that Compound No. 4, benzoyl monosulfide, is one of the few such monosulfides which showed vulcanization characteristics, and that the best properties were developed with a concentration of less than 1 per cent. Neither the zinc salt of Compound No. 1 nor the diphenylguanidine salt were vulcanizing agents.

GROUP V—*Thiocyanic sulfides*.—The sulfides shown in Figure 3 are probably polymers because of their high melting points and low solubilities. Com-

TABLE I
VULCANIZATION OF BUNA-S WITH ORGANIC SULFIDES

Group	Sulfide	Structure	Properties of vulcanizates
I	Aliphatic	$R-S_x-R$	No vulcanization
II	Aromatic	$Ar-S_x-Ar$	No vulcanization
III	Miscellaneous		Only the disulfide from pinene-thiol is of interest
IV	Acidic		Rate of cure slow, thiosulfonic acid sulfide yielded vulcanizate of low elongation but fair tensile strength
	Polythiodiacetic acids	$S_x(RCOOR)_2$	Only free acid sulfide yielded vulcanizate with acceptable stress-strain properties
V	Thiocyanic	$(NCS-S_x-SCN)_y$	Excellent heat resistance, high hysteresis, low rate of cut-growth
VI	Amine	$\begin{array}{c} R_2 \quad R_3 \\ \quad \\ R_1-N-S_x-N-R_4 \end{array}$	Excellent heat resistance, high hysteresis, rapid rate of cut-growth
VII	Thiuram	$\begin{array}{c} R_2 \quad R_3 \\ \quad \\ R_1-\text{NC}-S_x-\text{CN}-R_4 \\ \quad \\ S \quad S \end{array}$	Good heat resistance, low hysteresis, rapid rate of cut-growth
VIII	Phenolic		Excellent heat resistance, high hysteresis, low rate of cut-growth

pound No. 1 is quite insoluble in GR-S, and its melting point is above the vulcanizing temperature. It is seen also that, as the concentration increases, the moduli increase and elongation values decrease. Substitution of thionyl

GROUP III - MISCELLANEOUS SULFIDES

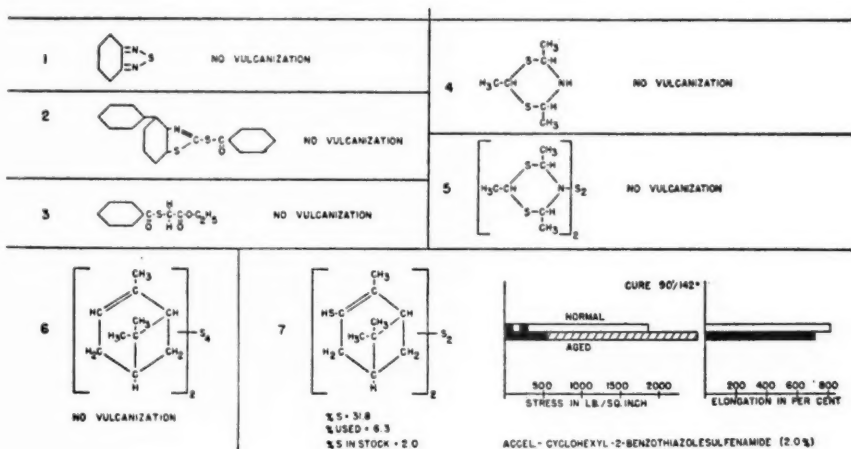


FIG. 1

TABLE II
BASE FORMULA

Buna-S (GR-S)	100
Carbon black (EPC)	40
Zinc oxide	3
Mineral rubber	4
Softener	4
Accelerator	As shown
Organic sulfide	As shown



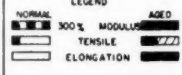
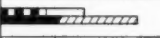
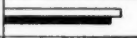
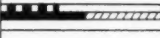


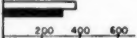
TABLE III
GROUP I—ALIPHATIC SULFIDES
STRUCTURE—R—S_x—R

Allyl sulfide
Allyl disulfide
Bis(2-hydroxyethyl) sulfide
tert-Butyl disulfide
tert-Butyl tetrasulfide
Dipropyl tetrasulfide
Dodecyl disulfide

TABLE IV
GROUP II—AROMATIC SULFIDES
STRUCTURE—Ar—S_x—Ar

Phenyl disulfide
Benzyl disulfide
2-Naphthyl disulfide
Triphenylmethyl tetrasulfide

GROUP IV - ACID SULFIDES

FORMULA	% S USED	% S STOCK	CURE	ACCEL	PHYSICAL PROPERTIES OF VULCANIZATE		
1 $\begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{S}_4 \\ \\ \text{CH}_2\text{COOH} \end{array}$	52.0	4.0	2.08	90/142°C	B		
2 $\begin{array}{c} \text{CH}_2\text{COO} \\ \\ \text{S}_4 \\ \\ \text{CH}_2\text{COO} \end{array} \text{Zn}$	41.4	5.0	2.07			SLIGHT VULCANIZATION	
3 $\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{CH}_2\text{CO-N}=\text{C} \begin{pmatrix} \text{N} \quad \text{H} \\ \quad \\ \text{C}_6\text{H}_4 \end{pmatrix}_2 \\ \\ \text{S}_4 \\ \\ \text{CH}_2\text{CO-N}=\text{C} \begin{pmatrix} \text{N} \quad \text{H} \\ \quad \\ \text{C}_6\text{H}_4 \end{pmatrix}_2 \\ \quad \\ \text{O} \quad \text{H} \end{array}$	20.4	10.0	2.04			SLIGHT VULCANIZATION	
4 $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}-\text{S}-\text{C} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	13.2	5.0	0.66	90/142°C	A		
5 $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}-\text{S}_2-\text{C} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	23.5	5.0	1.18	90/142°C	A		
6 $\begin{array}{c} \text{CH}_2-\text{S}-\text{C}-\text{S} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	43.7	5.0	2.18			NO VULCANIZATION	
7 $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}-\text{S}-\text{S}-\text{S}-\text{S}-\text{C} \\ \quad \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	46.8	4.0	1.87	90/142°C	B		
					STRESS - LB/SQ. INCH		ELONGATION - PER CENT

ACCEL

A- CYCLOHEXYL-2-BENZOTHAZOLESULFENAMIDE (2.0%)

B- TETRAMETHYLTHURAM DISULFIDE (0.5%)

ACCEL
A - CYCLOHEXYL-2-BENZOTHAZOLESULFENAMIDE (2.0%)
B - TETRAMETHYLTHURAM DISULFIDE (0.5%)

Fig. 2

GROUP V - THIOCYANIC SULFIDES

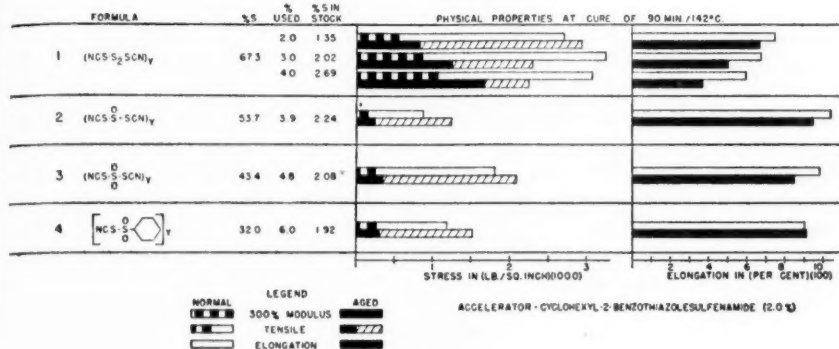


FIG. 3

or sulfonyl chlorides (Compounds No. 2 and No. 3) for sulfur monochloride results in a vulcanizate having poorer properties. The mixed sulfide from benzenesulfonyl chloride and ammonium sulfocyanide likewise gave vulcanizates of mediocre properties. All these vulcanizates showed markedly poorer properties when a thiuram disulfide accelerator was used. Hysteresis properties as shown by heat generation were very high, but resistance to flex-cracking was excellent.

GROUP VI - AMINE SULFIDES

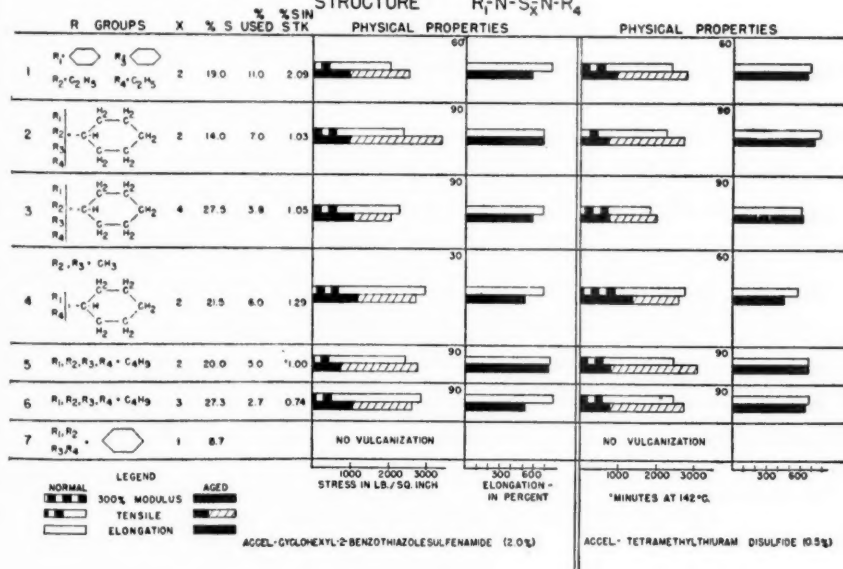


FIG. 4

GROUP VIII—*Phenolic sulfides*.—As vulcanizing agents the phenolic sulfides in general yielded vulcanizates which showed excessive heat generation, but excellent stress-strain, heat embrittlement, and flex-crack resisting properties. While our studies are in agreement with those of Wolf, Deger, Cramer and de Hilster², one compound—2-naphthol tetrasulfide—was found to differ markedly from the above mentioned characteristics in that some vulcanizates made from it exhibited nearly normal heat generation temperatures. Figure 6 shows the properties developed with three different percentages of 2-naphthol tetrasulfide, compared with a sulfur control. It is of note to mention the

GROUP VIII - PHENOLIC SULFIDES

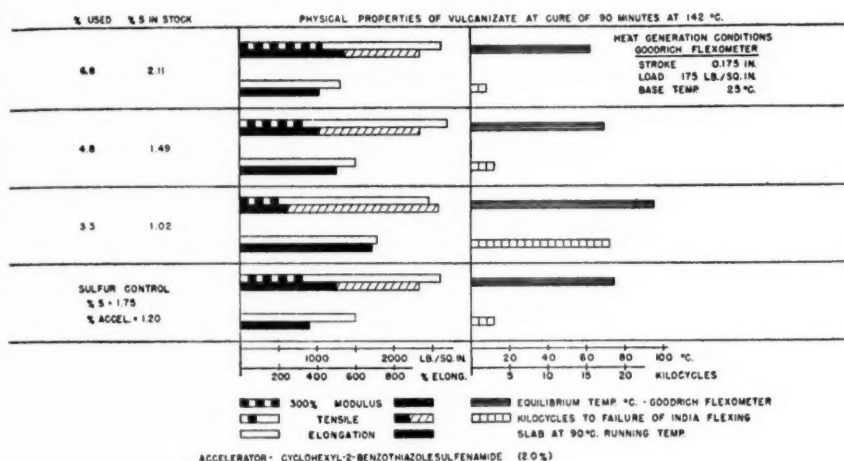
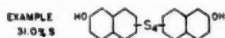


FIG. 6

unusual flexing properties of the stock containing 3.3 per cent of the sulfide. Unfortunately, heat generation was abnormally high with this stock.

In addition to 2-naphthol tetrasulfide, vulcanizing polysulfides were made from pyrocatechol, phenol, *o*- and *p*-chlorophenol, benzylphenol, *p*-nitrophenol and *o*-cresol. However, 4-*tert*-butyl-*m*-cresol and resorcinol polysulfides were quite insoluble in GR-S, and were not vulcanizing agents.

SUMMARY

Buna-S (GR-S) was vulcanized with acid, thiocyanic, amine, thiuram and phenolic sulfides. Heat embrittlement and resistance to cut-growth of the vulcanizates obtained with most of these compounds were better than those exhibited by normal stocks containing free sulfur, but heat generation was higher.

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AGING OF GR-S VULCANIZATES IN AIR, OXYGEN, AND NITROGEN *

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Temperature aging of rubber vulcanizates in the absence of oxygen has been studied by many workers. When oxygen is carefully excluded there is little change in physical properties, an indication that oxidation is the major factor in the aging of rubber vulcanizates. Jones¹ found no appreciable change in tensile strength and elongation after heating in a vacuum at 158° F (70° C) for 14 days. Kohman² heated rubber vulcanizates in both nitrogen and carbon dioxide at 80° C, and observed little decrease in tensile strength compared to the marked decrease obtained in oxygen. At an oven temperature of 90° C Reed³ found little deterioration either in a vacuum or in pure nitrogen, but in commercial nitrogen the aging was essentially the same as in air.

Little work of a comparable nature has been reported with respect to GR-S. In a recent paper Sturgis, Baum, and Vincent⁴ reported that they observed no significant difference in the results of aging GR-S vulcanizates in air and in purified nitrogen, at either 70° or 100° C, from the standpoint of modulus, tensile, elongation, and hardness values. They concluded that the hardening of GR-S vulcanizates by heat may be primarily due to some other cause than oxidation.

The object of the study reported here was to determine whether the changes in physical properties which occur during aging in the air oven and in the oxygen bomb are caused by oxygen. If so, the substitution of a nitrogen atmosphere should show significant differences. The aging of GR-S type vulcanizates has therefore been studied in oxygen and nitrogen at 80° C and 300 pounds per square inch, and in air and nitrogen at an oven temperature of 100° C.

A tread-type stock was employed, with the variations shown in Table I. The uninhibited GR-S employed in stocks A, B, and B' was prepared with the addition of 2 parts of sulfur as stabilizer to a GR-S latex in place of the usual antioxidant. After coagulation, the polymer was dried in a vacuum oven at 50° C. No antioxidant was employed in stock A. One part of antioxidant was added to stock B in order to observe the effect of the nitrogen atmosphere on the aging behavior of both inhibited and uninhibited GR-S stocks prepared from the same polymer. Stock B', identical to B, was studied at a later date to determine the reproducibility of the data and to extend the aging period in the bomb from 5 to 10 days. Table II shows good reproducibility of results for the aging of these two stocks. Stock C was included to determine whether the results obtained with the special polymer could be duplicated when approximately 2 parts of antioxidant were added to the latex in the usual manner.

A prepurified nitrogen containing less than 5 parts per million of oxygen

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was obtained from the General Electric Company. The samples to be aged in nitrogen were suspended in metal containers for oven aging and in bombs for aging under pressure. Nitrogen was passed through the aging chambers connected in series to displace the air. The system was then evacuated to remove as much as possible of the oxygen dissolved in and adsorbed on the samples. The alternate passage of nitrogen and evacuation was repeated several times, and finally a stream of nitrogen was passed through for several additional hours until analysis of the exit gas showed no detectable oxygen. An adaptation of the Winkler method⁵ was used for the analysis. With careful manipulation and the use of blank titrations, the method is capable of detecting as little as 0.01 per cent oxygen by volume.

After the air had been displaced as described above, the metal containers used for the oven aging were closed under a slight pressure of nitrogen (2 to 3

TABLE I
COMPOSITION OF STOCKS

Stock	A	B, B'	C
Uninhibited GR-S	100	100	...
Inhibited GR-S	100
Bardol	5	5	5
Fat acid	1.5	1.5	1.5
Channel black	50	50	50
Zinc oxide	5	5	5
Santocure	1.2	1.2	1.2
Sulfur	2 ^a	2 ^a	2
Phenyl- β -naphthylamine	...	1	2 ^a

^a Added to latex before coagulation

inches of water) sufficient to prevent any possible diffusion of air into the aging chamber. The closed containers were then placed in an oven at 100° C, along with an identical control set containing air under the same slight pressure. The nitrogen and oxygen bombs were filled to a pressure of 300 pounds per square inch and heated in a bath at 80° C.

BOMB AGING

The elongation, stress at 200 and 300 per cent elongation, and tensile strength after aging in oxygen and nitrogen at 80° C and 300 pounds per square inch are shown in Table IIA. Each value represents the average of three test-strips. The numbers in parentheses show percentage retention of the original value. The effect of nitrogen atmosphere on aging results is shown more clearly by the graphs prepared from these data.

The tensile strength after aging is compared with the initial values in Figure 1A. In nitrogen the tensile strength was essentially unchanged, except for stock C, which showed a small decrease after 10 days. In oxygen, however, the uninhibited material broke down rapidly so that after 5 days only 30 per cent of the original value was retained. Although inhibited stocks B, B', and C did not break down so extensively, the observed decrease in tensile strength is largely the result of oxidation. The fact that the tensile strength of the uninhibited material was unchanged in nitrogen is additional evidence that there was no significant amount of oxygen in the nitrogen employed.

The increase in stress at 200 per cent elongation obtained at 80° C was essentially the same in oxygen and nitrogen (Figure 2A). The stress at 300

TABLE II
AGING OF GR-S TYPE VULCANIZATES

	Stock	A. Bomb Aging, 80° C, 300 lbs. per sq. in.					B. Oven Aging at 100° C				
		Aging conditions Gas Days	Ultimate elongation (%)	Modulus (lbs. per sq. in.)		Tensile strength (lbs. per sq. in.) (%)	Aging conditions Gas Days	Ultimate elongation (%)	Modulus (lbs. per sq. in.)		Tensile strength (lbs. per sq. in.) (%)
				200%	300%				200%	300%	
A (uninhibited), 45-minute cure at 298° F		Initial	490	730	1300	2630	Initial	490	730	1300	2630
		O ₂ 2	295 (60)	1050	1560	1540 (58)	Air 2	170 (35)	1440 (55)
		5	80 (16)	800 (30)	5	120 (25)	1045 (40)
		N ₂ 2	380 (78)	1040	1900	2780 (106)	N ₂ 2	330 (67)	1250	2380	2720 (103)
		5	350 (72)	1160	2150	2620 (100)	5	315 (64)	1340	2395	2560 (97)
B (1% PBNA), 55-minute cure at 298° F		Initial	510	820	1380	2720	Initial	510	820	1380	2720
		O ₂ 2	440 (86)	1050	1710	2570 (95)	Air 2	275 (54)	1590	...	2490 (92)
		5	450 (88)	1050	1670	2440 (90)	5	210 (41)	1875	...	1980 (73)
		N ₂ 2	420 (82)	965	1800	2730 (100)	N ₂ 2	355 (70)	1150	2060	2590 (95)
		5	375 (74)	1090	2000	2650 (98)	5	320 (63)	1260	2320	2540 (93)
B' (same as B)		Initial	555	720	1280	2760	Initial	555	720	1280	2760
		O ₂ 5	435 (78)	1045	1665	2325 (84)	Air 2	290 (52)	1585	...	2525 (92)
		10	380 (69)	1110	1685	2040 (74)	5	210 (38)	2030	...	2180 (79)
		N ₂ 5	415 (75)	1040	1885	2850 (103)	N ₂ 2	380 (68)	1130	2025	2785 (101)
		10	380 (69)	1200	2130	2800 (101)	5	340 (61)	1220	2200	2630 (95)
C (2% PBNA), 50-minute cure at 298° F		Initial	615	790	1370	3290	Initial	615	790	1370	3290
		O ₂ 2	485 (79)	1125	1840	3030 (92)	Air 2	320 (52)	1590	2615	2805 (85)
		10	405 (66)	1400	2070	2625 (80)	5	290 (47)	1920	...	2920 (89)
		N ₂ 2	455 (74)	1065	1905	3180 (97)	N ₂ 2	395 (64)	2185	...	3020 (92)
		10	375 (61)	1310	2240	2915 (89)	5	360 (58)	1360	2365	2935 (89)

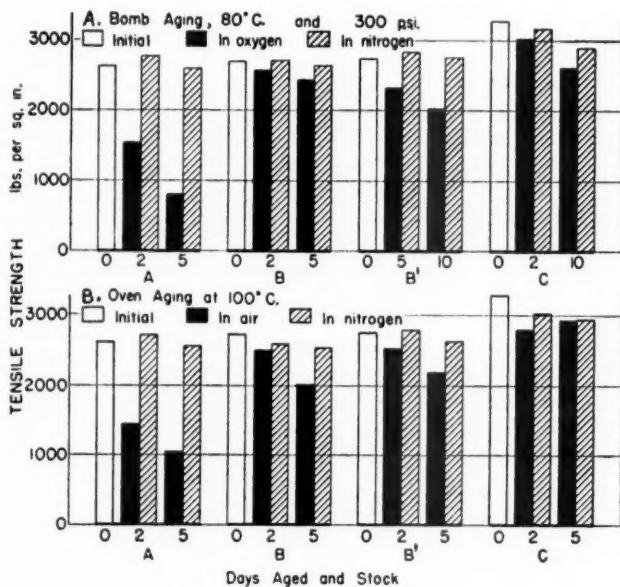


FIG. 1.—Effect of aging on tensile strength.

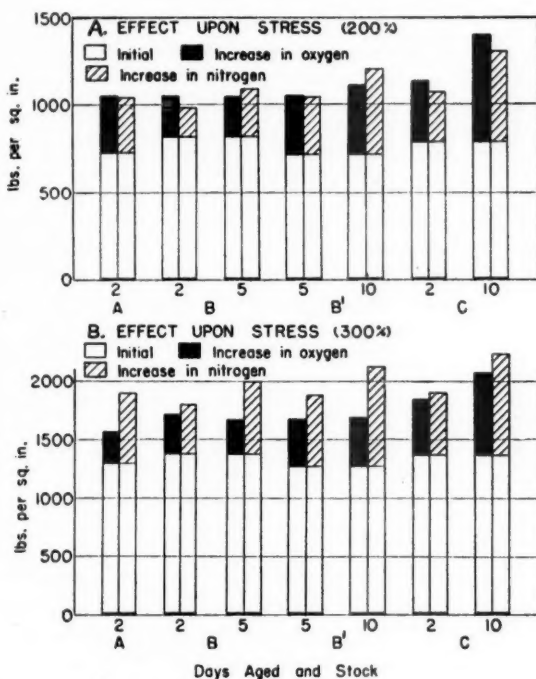


FIG. 2.—Effect of bomb aging in oxygen and nitrogen at 80°C and 300 pounds per square inch on stress.

per cent elongation (Figure 2B) actually increased more in nitrogen than in oxygen. One possible explanation would be that chain scission, as evidenced by the decrease in tensile strength in oxygen, would logically have a softening effect. At any rate it is apparent that the modulus increase obtained in the oxygen bomb at 80° C is not caused by oxygen in the aging atmosphere since an equal or greater increase was obtained in nitrogen. Most of the increase took place during the first 2 days of aging and remained relatively constant thereafter in oxygen, but increased slowly in nitrogen as shown for stocks B and B' in Figure 2B. The cause of the modulus increase at 80° C has not yet been determined, aside from the fact that it is not due to oxygen in the aging atmosphere.

The elongation values in Table IIA show little difference between the decrease obtained in oxygen and nitrogen in the case of the inhibited stocks. The uninhibited material, however, shows considerably better retention of elongation in nitrogen. The greater decrease in ultimate elongation in oxygen, together with the extensive tensile breakdown, may be attributed to a reaction with oxygen which leads to chain scission.

OVEN AGING

The data for oven aging at 100° C in air and in nitrogen are presented in Table IIB. The tensile strength values from this table are compared in Figure 1B, which shows the same relation obtained in the oxygen bomb—namely, little change in the presence of nitrogen but a definite decrease after aging in air. The difference between the results in air and nitrogen becomes less as the concentration of antioxidant increases, as shown by the extensive breakdown obtained with uninhibited stock A; B and B' with 1 part and C with 2 parts of antioxidant show progressively less deterioration.

The stiffening or hardening of the vulcanizates, as measured by modulus increase, was drastic in air at 100° C, as shown by the black bars in Figure 3.

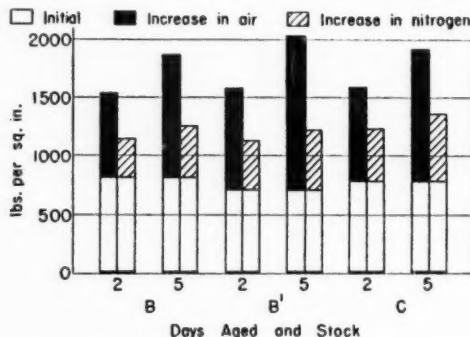


Fig. 3.—Effect of oven aging at 100° C in air and in nitrogen upon stress at 200% elongation.

After 5 days the stress at 200 per cent elongation was more than doubled in every case. In nitrogen, however, the modulus increased only to about the same extent as in the bomb. If we attribute the increase observed in nitrogen to other factors, then the additional increase obtained in air represents the hardening due to the action of oxygen. On this basis more than half of the observed hardening of GR-S vulcanizates after 5 days of aging in air at 100° C may be attributed to the action of oxygen.

The ultimate elongation was much better after aging in nitrogen than in air at 100° C (Table IIB). Since the elongation reflects changes in both tensile and modulus, these values confirm the observation that oxygen plays an important part in the aging of GR-S in the air oven at 100° C.

The results obtained by the aging of GR-S type vulcanizates in air and nitrogen at 100° C are not in agreement with the work of Sturgis, Baum, and Vincent³, who reported the same amount of hardening upon heating in air and nitrogen. Their stock was the same as stock C in Table I except for the softeners and accelerator employed. This may have contributed to the difference in the results.

CONCLUSIONS

The results of aging GR-S vulcanizates in air, oxygen, and nitrogen show:

1. The decrease in tensile strength observed in both bomb and oven aging is caused by the action of oxygen.
2. The modulus increase obtained in the oxygen bomb at 80° C is not caused by oxygen in the aging atmosphere.
3. At 100° C in air, more than half of the hardening, measured by the modulus increase obtained after five days, may be attributed to the action of oxygen.

It therefore appears that oxygen acts on GR-S vulcanizates in two distinctly different ways:

1. A reaction leading to tensile breakdown, which no doubt involves chain scission. This reaction takes place at both 80° and 100° C, and is effectively retarded by the antioxidant, phenyl- β -naphthylamine.

2. A reaction producing a stiffening of the GR-S, as shown by the modulus increase. This stiffening suggests the formation of polymeric products—for example, by cross-linkage. This reaction was not observed at 80° C, but was a major factor in the aging at 100°, and was little affected by the antioxidant employed.

ACKNOWLEDGMENT

The authors wish to express their thanks to The Firestone Tire & Rubber Company for sponsoring this work and to O. D. Cole for helpful suggestions and cooperation.

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- ³ Reed, *Ind. Eng. Chem.* **21**, 316 (1929).
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- ⁵ Winkler, *Ber.* **21**, 2843 (1888).

PIGMENT INCORPORATION IN GR-S THROUGH LATEX *

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The physical properties of GR-S gum stock are decidedly inferior to those of natural-rubber gum stock, and they have to be greatly enhanced for practical use of the elastomer. At present these physical properties are augmented to the greatest degree by compounding with reinforcing pigments, especially carbon blacks. Furthermore, experience has shown that, for a given pigment, the reinforcement it affords is proportional to the degree to which it is dispersed in the elastomer. A thorough dispersion of pigment on the mill or in the Banbury mixer is not feasible with schedules which can be applied in the factory, particularly with those pigments which are more difficult to disperse.

A study of the relation between the characteristics of pigments used as fillers in GR-S and their reinforcing properties indicated that the particle size of the pigment was the predominant characteristic associated with reinforcing ability. The finer carbon blacks yielded the greatest reinforcement, measured by ultimate tensile strength; also, a fine grade of magnesium oxide yielded compounds with tensile strengths approximately equal to stocks made with blacks of the same particle size. Stocks made from a coarser magnesium oxide were considerably lower in tensile strength, and zinc oxides and calcium carbonates fell roughly in the order of their particle sizes. The calcium carbonates, zinc oxides, and magnesium oxides had to be worked on the mill much more than the carbon blacks to develop maximum reinforcement; and, even though well worked, the finest zinc oxide and calcium carbonate did not yield compounds with properties which their particle size indicated they should have. It was felt that this was due to inability to disperse these materials properly on the mill; thus their effective particle size in the compound was much greater than their ultimate size.

Accordingly, a better means was sought to disperse fillers in GR-S than that afforded by milling. It was known that excellent dispersions of pigments could be made in water with the aid of dispersing agents. It was also reported that the polymer particles in GR-S latex were very finely divided, less than one-tenth the diameter of particles in natural rubber latex. If, then, a water suspension of well dispersed pigment was mixed with latex, and the filler and polymer were precipitated or coagulated simultaneously, it was thought that the pigment might be more thoroughly dispersed in polymer than it would be through dry milling; the physical properties of compounds made in this manner should then show improvement over those made on the mill.

INCORPORATION OF PIGMENTS IN LATEX

A practical method follows for incorporating reinforcing pigments in GR-S polymers while the latter is in the latex stage. A high degree of dispersion is

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attained which is reflected in compounds with physical properties well above those of identical compounds made on the mill:

The pigment is dispersed, with the aid of a colloid mill or ball mill, in water containing a suitable dispersing agent. The type of dispersing agent employed depends on the pigment to be dispersed. For example, the material known as Daxad No. 23 is excellent for dispersing zinc oxides or whittings, whereas Daxad No. 11 is a somewhat more effective dispersing agent for carbon blacks. A concentrated slurry is first prepared and then passed through the mill until the pigment is thoroughly dispersed. This slurry should contain 5 to 10 volumes of pigment per 100 volumes of water, depending on the fineness of the pigment; the finer the particle size, the smaller the volume of pigment. The thoroughness of dispersion is important, and may be checked with an ultramicroscope or other convenient means.

This slurry is then diluted with an equal volume of water and thoroughly mixed with an amount of GR-S latex containing the weight of polymer which will yield the desired ratio of pigment to polymer.

TABLE I
PHYSICAL DATA ON CARBON BLACK COMPOUNDS

Compound no.	1	2	3	4	5	6
GR-S	100.00	100.00	100.00	100.00	100.00	100.00
EPC black (40 m μ)	50.00	50.00	50.00	50.00
Fine channel black (30 m μ)	50.00	50.00
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00
Mercaptobenzothiazole	1.50	1.50	1.50	1.50	1.50	1.50
Softener (Bardol)	5.00	5.00	5.00	5.00	5.00	5.00
Softener (Turgum)	10.00	10.00
Filler dispersed	In latex	On mill	In latex	On mill	In latex	On mill
	Cure at 293° F (min.)	Tensile strength (lbs. per sq. in.)	Stress at 300% elongation (lbs. per sq. in.)	Elongation at break (%)	Torsional hysteresis (K)	
Compound 1	40	3460	1270	580	...	
	50	3640	1680	510	0.148	
	60	3230	1890	440	...	
Compound 2	40	3200	1060	625	...	
	50	3245	1160	580	0.164	
	60	3115	1215	530	...	
Compound 3 ^a	50	3440	520	805	...	
	60	3650	630	775	...	
	75	3825	725	730	0.145	
Compound 4 ^b	60	2545	400	850	...	
	80	2750	505	795	...	
	90	2960	585	745	...	
	120	3235	775	725	0.211	
Compound 5	80	3285	1100	625	...	
	100	3615	1100	635	0.224	
	120	3540	1195	620	...	
Compound 6	40	3250	1050	610	...	
	50	3315	1320	550	0.183	
	60	3200	1300	525	...	

^a Cut growth, inch (cycles): at 75-min. cure, 0.6 (30,000); at 90-min. cure, 0.66 (25,000).

^b Cut growth, inch (cycles): at 50-min. cure, 0.91 (30,000); at 60-min. cure, 0.81 (25,000).

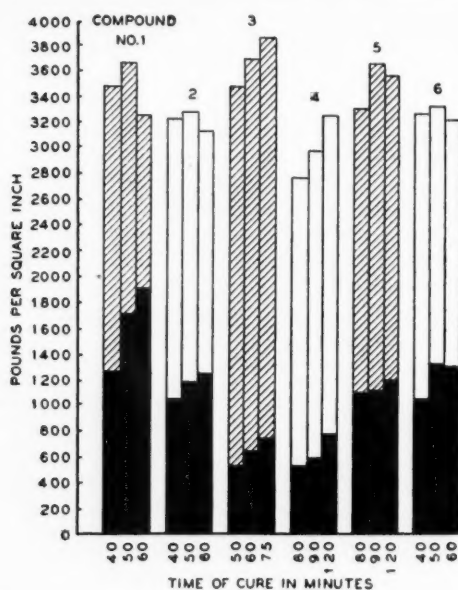


Fig. 1.—Stress-strain properties of carbon black compounds.

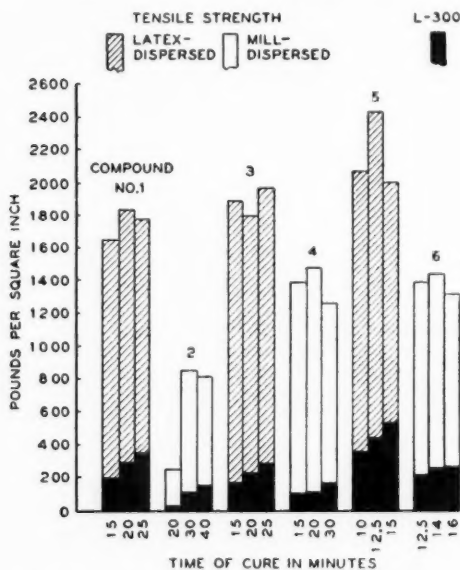


Fig. 2.—Stress-strain properties of zinc oxide compounds.

The mixture is coagulated with dilute sulfuric acid (25 volumes of concentrated sulfuric acid plus 475 volumes of water) or 2 per cent alum solution. As the coagulant is added, a porous mass of polymer and pigment forms, which, on continued addition of the reagent, breaks up into a fine crumb.

TABLE II
 PHYSICAL DATA ON ZINC OXIDE COMPOUNDS

Compound no.	1	2	3	4	5	6
GR-S	100.00	100.00	100.00	100.00	100.00	100.00
Coarse zinc oxide (350 m μ)	100.00	100.00
Medium fine zinc oxide (190 m μ)	100.00	100.00
Fine zinc oxide (120 m μ)	100.00	100.00
Stearic acid	2.00	2.00	2.00	2.00	2.00	2.00
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00
2-Mercaptothiazoline	1.00	1.00	1.00	1.00	1.00	1.00
Aldehydeamine	0.25	0.25	0.25	0.25	0.25	0.25
Filler dispersed	In latex	On mill	In latex	On mill	In latex	On mill
	Cure at 282° F (min.)	Tensile strength (lbs. per sq. in.)	Stress at 300% elongation (lbs. per sq. in.)	Elongation at break (%)	Torsional hysteresis ^a (K)	
Compound 1	15	1660	205	950
	20	1840	295	810	0.096	...
	25	1780	350	730
Compound 2	20	265	40	1475
	30	865	120	1030
	40	830	165	790
Compound 3	15	1900	190	895	0.096	...
	20	1790	240	765
	25	1960	300	740
Compound 4	15	1395	115	1015
	20	1480	125	855	0.122	...
	30	1280	185	695
Compound 5	10	2075	370	750
	12.5	2440	450	735	0.088	...
	15	2000	540	585
Compound 6	12.5	1395	220	780
	14	1440	260	735
	16	1325	265	665

^a Method of Mooney and Gerke (RUBBER CHEM. TECH. 14, 35 (1941)). Determinations were made through courtesy of F. L. Holbrook, U. S. Rubber Company.

^b Hysteresis of this cure could not be measured at 282° F, because its modulus was too low at that temperature.

Care must be taken to add sufficient coagulating agent, otherwise filtration is difficult. The crumb is filtered and washed free of water-soluble impurities. The material can be repulped readily while wet, and washed with hot water to aid in removing impurities.

The master batch may be dried in an air dryer at 70° C, and is then ready to be compounded with sulfur, accelerators, etc.

The process has been employed in this laboratory to make master batches of carbon blacks, zinc oxides, and calcium carbonates. Stocks have been prepared with these master batches and various properties have been measured.

CARBON BLACK COMPOUNDS

Compounds were prepared with a fine channel black and an easy-processing carbon. The physical data are given in Table I. Compounds of the same

recipe which were made by dispersing the pigment on the mill are included for comparison. It is evident in Figure 1 that the stress-strain properties of the latex-dispersed stocks are of a higher order than those of the mill-dispersed. The hysteresis values of compounds 1 and 3, compared with those of compounds 2 and 4, indicate that the heat build-up of these latex-dispersed stocks should be lower than that of mill-dispersed; this order is reversed for HPC black compounds 5 and 6. The comparison of cut growth of compounds 3 and 4 shows that the latex-dispersed compound is superior in this respect also.

ZINC OXIDE COMPOUNDS

Three different zinc oxides were used to make master batches—a fine, a medium fine, and a coarse grade. The physical properties of stocks made with these master batches and also those of compounds of the same recipe which were mill-dispersed are given in Table II. Figure 2 shows that the stress-strain properties of the latex-dispersed compounds are markedly higher than those of the mill-dispersed. The hysteresis of the former is lower than that of the latter, another indication that the heat build-up of the latex-dispersed stocks should be less than that of the mill-dispersed. The electrical properties of compounds 5 and 6 were measured, and are shown in Figure 3.

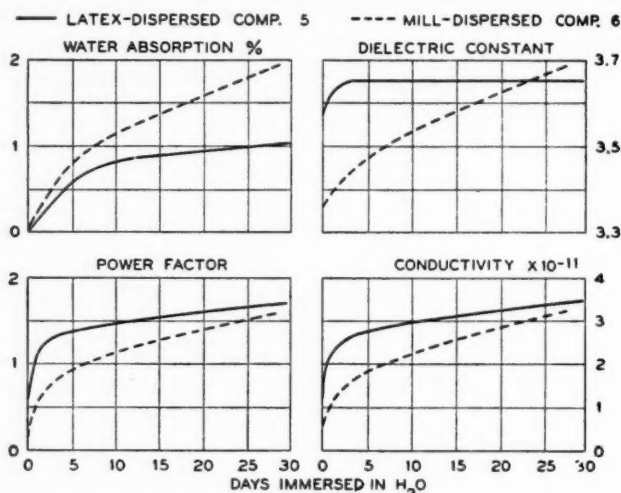


Fig. 3.—Electrical properties of zinc oxide compounds 5 and 6.

The mill-dispersed compound possesses better electrical properties initially, but during immersion in water they decline more rapidly than those of the latex-dispersed compound, which, therefore, has the advantage of greater stability.

CALCIUM CARBONATE COMPOUNDS

To typify the improvement obtained by dispersing whittings in GR-S latex, a group of three particle sizes are cited—extra fine, fine, and moderately fine. Table III and Figure 4 show that a substantial improvement in stress-strain characteristics is obtained, compared with the mill-dispersed compounds. Furthermore, Figure 5 indicates that the electrical properties of a latex-

dispersed whiting compound are superior in all respects to those of the same compound dispersed on the mill.

The mill-mixed controls used for comparison were carefully prepared in the laboratory. It is unlikely that physical properties as good as these would be obtained in the factory. On the other hand, a latex-dispersed master batch in which the pigment is already well dispersed should yield compounds in the factory with physical properties substantially as good as those of a laboratory-prepared stock; it is generally recognized that sulfur, accelerators, etc., are less

TABLE III
PHYSICAL DATA ON CALCIUM CARBONATE COMPOUNDS

Compound no.	1	2	3	4	5	6	7	8
GR-S	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Extra fine CaCO ₃ (100 mμ)	95.00	95.00	125.00	125.00
Fine CaCO ₃	125.00	125.00
Medium fine CaCO ₃ (600 mμ)	91.00	91.00
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Stearic acid	2.00	2.00	2.00	2.00	1.00	1.00	1.00	1.00
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
2-Mercaptobenzothiazole	1.00	1.00	1.00	1.00
Aldehydeamine	0.25	0.25	0.25	0.25
Paraffin	2.00	2.00	2.00	2.00
Akroflex-C	1.00	1.00	1.00	1.00
Agerite White	1.00	1.00	1.00	1.00
Heliozone	2.00	2.00	2.00	2.00
Softener (Turgum)	10.00	10.00	10.00	10.00
Ethyl selenac	1.00	1.00	1.00	1.00
Altax	1.50	1.50	1.50	1.50
Filler dispersed	In latex	On mill	In latex	On mill	In latex	On mill	In latex	On mill
	Cure at 282° F (min.)		Tensile strength (lbs. per sq. in.)		Stress at 300% elongation (lbs. per sq. in.)		Elongation at break (%)	
Compound 1	12.5		1800		260		855	
	15		1995		325		830	
	20		2110		415		755	
Compound 2	15		1730		190		950	
	20		1770		220		850	
	30		1670		240		760	
Compound 3	80		965		85		1060	
	120		1120		125		895	
	150		1175		105		915	
Compound 4	15		690		85		870	
	20		700		110		725	
	30		620		170		630	
Compound 5	16		1850		290		780	
	17.5		1990		330		715	
	20		1985		400		645	
Compound 6	14.5		1270		145		930	
	17.5		1500		280		635	
	20		1400		355		540	
Compound 7	10		1210		180		900	
	11.5		1555		280		715	
	13		1475		315		615	
Compound 8	12		1010		170		875	
	13		1100		235		725	
	14		1035		285		615	

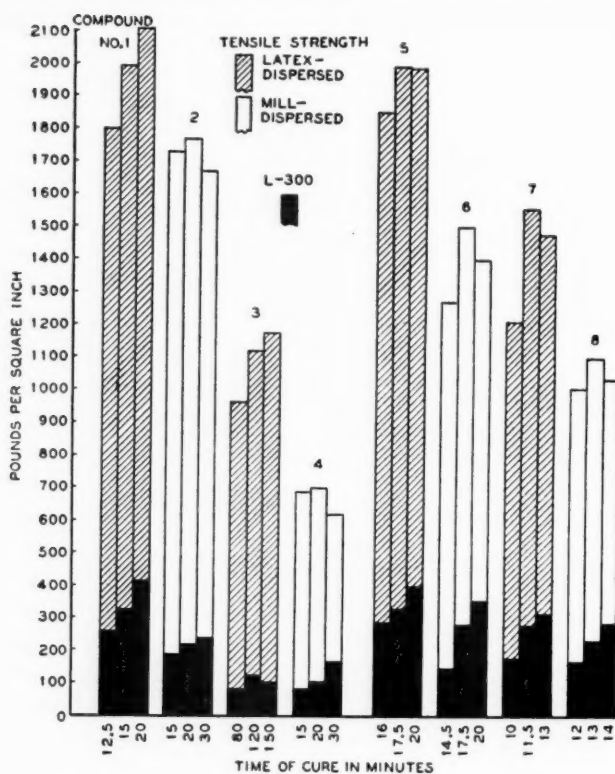


Fig. 4.—Stress-strain properties of calcium carbonate compounds.

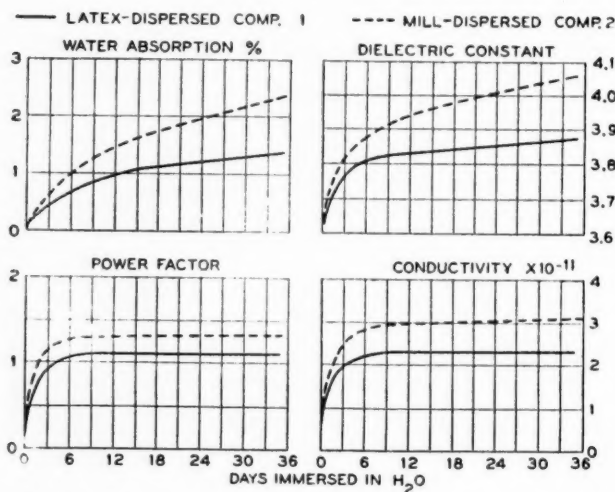


Fig. 5.—Electrical properties of calcium carbonate compounds 1 and 2.

difficult to disperse in polymer than is pigment. This is substantiated by a laboratory experiment in which two zinc oxide stocks were made with the same master batch. One was milled only 13 minutes and not refined; the other was milled 30 minutes and refined twice. The physical properties of the two compounds were substantially the same.

It is also practical to use a latex-dispersed master batch of high pigment-loading, and to cut back with polymer to make compounds of any desired loading. Compounds made in this manner may be slightly inferior to those made with master batches containing the desired loading for the compound which are not cut back. However, they are still greatly superior to the mill-mixed.

ACKNOWLEDGMENT

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INCORPORATION OF CARBON BLACK INTO GR-S LATEX ON A PRODUCTION SCALE *

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During the period from 1910 to 1920 the value of carbon black in imparting superior wear resistance to rubber goods was first recognized and utilized commercially. This new use resulted in the development of specialized types of carbon blacks for the rubber industry. Following 1920 the use of carbon black as a reinforcing agent for rubber became firmly established as part of the accepted compounding art. When synthetic rubbers came into general use it was found that the incorporation of carbon black was even more essential in obtaining quality than was the case with natural rubber. Unlike natural rubber, synthetic rubbers of the GR-S type are not capable of giving high quality pure-gum stocks or high-grade light-colored stocks. GR-S must be reinforced with carbon black or with a mixture of carbon black and other pigments if its physical properties are to be adequate for hard usage.

The replacement of natural rubber by GR-S is further complicated by the inherent resistance of GR-S to breakdown by milling. Crude natural rubber is normally a tough, elastic material, which changes to a soft, plastic substance when masticated in air. GR-S, on the other hand, while initially softer than natural rubber, does not show comparable breakdown characteristics. To make GR-S processable, higher temperatures are required, as well as longer milling times. Even with increased times and higher temperatures of milling, GR-S cannot be satisfactorily processed on existing equipment without the use of large amounts of softeners.

Because of these difficulties in breaking down GR-S, it was estimated early in the conversion program that GR-S would require at least 10 per cent more milling capacity than natural rubber. As a result of this need for increased tires and other rubber goods at the very time these products were most needed in the war effort. To offset this calculated loss of production, considerable sums were made available for an increase in milling equipment. Now, having acquired the necessary machinery, the industry finds itself hard-pressed to obtain the men necessary to keep the equipment in operation.

Since carbon black was known to be necessary for good physical properties of GR-S, and since GR-S was available in large quantities as a latex, it was obvious to try to mix the two. Many foreign and domestic patents and publications¹, including a ten-year old British patent, disclose the mixing of carbon black, pigmenting materials, and compounding ingredients with natural and synthetic rubber latex. Carbon black, pigmenting materials and compounding ingredients have been added to natural rubber latex to make commercially produced pigmented products by deposition, but in such products the rubber was not reinforced by the carbon black.

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From the study of many patents and of much literature on these matters, it was evident that helpful and important economies would result if carbon black could be added to GR-S latex on a production scale and a uniform dispersion of the carbon black within the rubber be obtained. Realizing the tremendous benefits to the industry and to the war effort that would follow from a solution of these problems, the General Tire & Rubber Company decided to enter this field and attempt a commercial solution of the problem.

LABORATORY INVESTIGATION

There are a number of ways to add carbon black to latex which appeared to promise success, but most of these presented technical difficulties. The direct addition of dry carbon black to latex did not ordinarily give a good dispersion of black, and usually caused partial coagulation of the latex. The use of a wetted black or of a slurry of black in water alone caused trouble, with agglomeration of the black in the rubber which was difficult to disperse. Handling problems were also increased, since a water slurry with carbon black (easy processing channel) of a content higher than 10 per cent is unworkable, and the black settled out from the latex mixture too fast to be practical in the available equipment. However, a good dispersion of carbon black which reduced these tendencies and one which blended readily with latex was obtained by the use of proper dispersing agents. The dispersion was readily made by mixing carbon black, water and dispersing agent, and grinding them together in a ball mill or colloid mill.

The most specific dispersing agents for carbon black can apparently be divided into three classes: (1) condensation products of naphthalenesulfonic acid and formaldehyde, such as Darvan 1, Daxad 11, Tamol R, etc.; (2) lignin-sulfonic acids or salts, such as Hornkem No. 1, Marathon Agent 340-2, etc.; and (3) glucoside extracts, such as Hornkem No. 12, quebracho extract, tannin extract, etc.

The carbon blacks to be dispersed present individual problems because of particle size, state of aggregation and the character of the surfaces, as well as the nature of the adsorbed gases. A rough test for the dispersing power of any agent can be obtained by making a heavy paste of unpelletized carbon black and water on a glass plate and determining the total amount of dispersing agent and water required to transform a stiff paste to a fluid mixture. For final selection of the best from a group of good dispersing agents, it is recommended that viscosity and settling tests be made on slurries containing various amounts of black, dispersing agent and water. This sort of test indicated that quebracho extract, Daxad 11, Darvan 1 and Tamol R were suitable dispersing agents for the ordinary types of carbon black.

For commercial and economic reasons it is important to use the minimum amount of dispersing agent to give a reasonably stable slurry that will blend readily with the latex. This minimum concentration of dispersing agent was found from a series of experiments in which different amounts of dispersing agents were used to stabilize carbon black slurries made in a colloid mill. It was immediately evident that very low amounts of dispersing agent were insufficient to promote fluidity and freedom from settling in a reasonably concentrated slurry (20 to 25 per cent solids). On the other hand, excessive amounts of dispersing agent tended to cause the formation of too many fines on coagulation and the loss of considerable black in the mother liquor. Black rubbers compounded to the formula shown in Table I were milled and tested. The results of these physical tests are shown in Table II.

TABLE I
COMPOUNDING FORMULA

Polymer	100
EPC black*	45
Zinc oxide	5
Sulfur	1.7
Santocure	1.2
Stearic acid	2.5
BRT No. 7	5

* Black dispersed in latex or on mill as indicated

TABLE II
EFFECT OF VARYING PROPORTIONS OF DAXAD NO. 11

Daxad No. 11 % on black	Cure at 292° F (min.)	Tensile strength (lbs. per sq. in.)	Stress at 300% elongation (lbs. per sq. in.)	Elongation at break (%)
0*	25	2270	535	705
	50	2370	800	575
	75	2630	920	570
0 ^a	25	1910	350	860
	50	2615	745	660
	75
1 ^a	25	1370	220	880
	50	2530	690	660
	75	2630	800	570
3	25	970	170	1010
	50	2445	340	780
	75	2525	495	720
6	25	1435	250	865
	50	2610	585	700
	75	2480	660	620
10 ^b	25	1915	600	880
	50	2620	580	720
	75	2370	730	640
14 ^b	25	1125	165	1000
	50	2475	455	765
	75	2875	620	700

* Control batch, black added on mill.

^a Viscous slurry in water.

^b Incomplete retention of black on coagulation and washing because of excessive dispersing agent.

An examination of the data in Table II indicates that no better physical properties result from the use of increased amounts of dispersing agent. Therefore, the use of the lowest amount of this type material which would give the best handling is indicated. Most of the subsequent work was done on a system containing 75 parts water, 25 parts carbon black and 0.75 parts Tamol R. This type of dispersion is still fluid and has little tendency to settle out.

Early in our investigation it was necessary to determine the effect of increasing the degree of dispersion of the carbon black in the water slurry on the physical properties of rubber. By preparing dispersions with high percentages of dispersing agents and doing considerable work on the dispersion by running it through a closely set colloid mill several times, excellent black

dispersions were obtained. Other dispersions were made with decreasing percentages of surface active materials and with less mechanical grinding. The extreme was to use no dispersing agent, and to run the black and water one pass through a colloid mill. When these various dispersions were mixed with latex and coagulated, the physical properties of the cured rubber mixes were very similar, and did not reflect the extreme differences in the degree of dispersion of the black in the water.

The conclusion we reached from this particular work was that, if the size of the aggregates of carbon black were considerably less than some definite maximum (less than the bead size) when deposited with the rubber, the shearing action of a pass or two through a mixing mill was sufficient to give good dispersion. For our subsequent work, uncompressed black was stirred into water and dispersing agent with simple stirring, thus eliminating entirely the use of colloid mills and ball mills.

Another method has been advocated with considerable advantage listed for it. The black in this method was dispersed in the normal way and then flocculated with alum. After flocculation, the alum was neutralized with a base. This flocculated black was then mixed with the latex and coagulated in the standard way. It is claimed that this flocculated black gives more stable suspensions in water and has less tendency to settle out than the type of dispersion described above and has less tendency to "bleed out" from the rubber.

The coagulation of a mixture of black and latex may be accomplished in numerous ways. Acid alone; a mixture of salt and acid; mixtures of salt, acid and alum; alum alone and zinc chloride alone² have all been used successfully as coagulating agents. Coagulation of the black latex is best accomplished by the use of some sort of rapid, one-step coagulation rather than the conventional method used for GR-S. This type of "shock" coagulation is best suited to entrap all the black in the coagulated rubber, and to produce a clear mother liquor. Table III shows a summary of some of the methods of coagulation

TABLE III
EFFECT OF DIFFERENT METHODS OF COAGULATION

Coagulating agent	% Agent on rubber-black solids	Cure at 292° F (min.)	Tensile strength (lbs. per sq. in.)	Stress at 300% elongation (lbs. per sq. in.)	Elongation at break (%)
Sulfuric acid	2*	25	2260	330	895
	...	50	2140	650	595
	...	75	3080	750	670
Sulfuric acid	1	25	2620	470	800
Sodium chloride	15*	50	3220	660	705
	...	75	2900	735	650
Alum	1	25	2800	570	715
Sulfuric acid	1	50	2850	720	650
Sodium chloride	15	75	3240	850	630
Alum	4.5	25	2400	515	705
	...	50	2640	710	650
	...	75	2900	755	625
Zinc chloride	4	25	835	115	1085
	...	50	2645	405	805
	...	75	3200	570	760

* Higher percentage recommended for satisfactory coagulation

which have been tried. From the data in this table it is clear that little change in the physical properties of these stocks is caused by the coagulation method and that the actual choice of a method must depend on operating conditions in the plant.

Because of its open, porous structure, the black pigmented crumb is readily dried. From time to time in the early part of this work it was observed that certain dried samples did not possess good physical properties, whereas others of apparently the same character had superior characteristics. Further investigations and a study of these samples indicated that the presence of moisture during milling brought the curing rate at least up to normal, and gave superior properties to the compound. These effects on the properties of the rubber are shown in Table IV. After this observation, it was found that the retention

TABLE IV
EFFECT OF MOISTURE

Sample	Bone dry			Moist		
	Tensile strength (lbs. per sq. in.)	300% modulus (lbs. per sq. in.)	Elongation (%)	Tensile strength (lbs. per sq. in.)	300% modulus (lbs. per sq. in.)	Elongation (%)
1	1520	450	690	2720	560	710
2	1775	395	760	2830	1030	590
3	995	220	920	2980	745	670
4	1560	275	925	2600	595	755
5	1310	835	420	2360	690	735

All samples were cured 50 minutes at 292° F

of moisture in the milled coagulum eliminated the previously unexplainable differences in quality of comparable cured stocks and produced uniformly good physical properties.

In summary it may be said that laboratory work on this problem showed that it was possible to make a cheap, satisfactory slurry of carbon black, that this slurry could readily be mixed with latex, and that the mixture could be coagulated to produce a black rubber with properties at least as good as those of GR-S into which carbon black had been incorporated by the conventional mill method. These developments made it desirable to try the process on a commercial scale.

PRELIMINARY PRODUCTION SCALE OPERATIONS

During the early part of March of this year the first incorporation of carbon black into latex on a production scale was made at the Government GR-S plant at Baytown, Texas, operated by the General Tire & Rubber Company and General Latex, Inc. Six runs of some 10,000 pounds each were made, using different types and amounts of dispersing agents, different carbon blacks, and variations in plant handling. Both the flocculated and dispersed types of carbon black slurry were successfully blended with latex at this time. This work indicated that the system was adaptable to existing plant processing equipment with minor changes. A brief description of these runs is listed in the table below:

Run no.	1	2	3	4	5	6
Carbon black	W-6	Statex-93	W-6	W-6	W-6	W-6
Dispersing agent	Daxad-11	Daxad-11	Quebracho	Daxad-11	Daxad-11	Daxad-11
% Dispersing agent on black	4.2	2.7	4.0	4.2	4.2	3.0

Plant scale runs required a carbon black slurry which could be rapidly prepared with a minimum of equipment and mechanical work, possessing sufficient fluidity to be readily pumped, and stable enough to prevent settling under handling conditions. In the initial work, uncompressed black was added to the dispersing agent solution in a tank agitated by a Lightnin' Mixer. The rate of wetting of the black determined the speed at which it could be added.

The method of coagulation of the dispersed carbon black-latex mixture differed from that of standard GR-S mainly in the elimination of the creaming step and the use of "shock" coagulation of the black and the rubber. Using salt and acid for coagulation, it was found desirable to use higher concentrations of both salt and acid than are normal in present plant practice, and to use them concurrently. This was the case since it was preferable that the black and rubber be "set" as instantaneously as possible. A small amount of alum in conjunction with acid and salt materially reduced the required quantities of the latter. It was found that the most effective method of controlling crumb size and eliminating fines was to avoid excessive agitation during coagulation.

The black pigmented rubber crumb obtained from the coagulation was easily dewatered and sufficiently dried in conventional equipment. The drying rate of the pigmented crumb was faster than normal because of its porous structure. In continuous plant operation it should be possible to effect a substantial reduction in the drying cycle. Furthermore, the crumb did not tend to stick or gum-up the dryer apron. Thus, delays in plant production due to shutdowns for cleaning the dryers should be minimized.

Although the resulting pigmented rubber crumbs can be baled readily and packed in the conventional manner, it is probable that some savings in packaging costs will be made possible by the firmness of the bale of black rubber. A standard size bale of black rubber weighs about 90 pounds rather than 75 pounds which is the conventional weight for a bale of GR-S.

FACTORY PROCESSING AND PHYSICAL TESTS

Factory evaluation studies on commercial latex-mixed black rubber were made by using the factory tread formulations and the mixing technique ordinarily used for GR-S in General Tire's Akron plant. The mixing times of the

TABLE V
COMPOUNDING RECIPES

Stock no.	1	2	3	4
Rubber	100	100	100	100
W-6 black	45	45
Statex-93 black	52	48*
Zinc oxide	3.0	3.0	3.0	3.0
Sulfur	1.7	1.7	1.7	1.7
Santocure	1.3	1.3	0.8	0.8
Stearic acid	1.0	1.0	2.0	2.0
Stabilite	0.5	0.5	0.3	0.3
Turgum	3.0	3.0
Bardol	4.0	4.0	3.0	3.0
Pine tar	3.5	3.5	2.0	2.0
B.L.E.	0.3	0.3	0.3	0.3
Black added	On mill	In latex	On mill	In latex

* % Carbon black by analysis of latex masterbatch

TABLE VI
MIXING PROCEDURE FOR FACTORY BANBURY BATCHES

GR-S Control Tread Stock

- (1) Add crude rubber and Turgum, and run to 4 minutes.
- (2) Add dry black, and run to 9 minutes.
- (3) Add dry ingredients, except Santocure, and run to 11 minutes.
- (4) Add oils, and run to 14 minutes.
- (5) Add Santocure, and run to 15 minutes.
- (6) Dump for a total time of 17 minutes.
- (7) Add sulfur on open mill.

Latex-Black Tread Stocks

- (1) Add black masterbatch and Turgum, and run to 2 minutes.
- (2) Add dry ingredients, except Santocure, and run to 4 minutes.
- (3) Add oils, and run to 7 minutes.
- (4) Add Santocure, and run to 8 minutes.
- (5) Dump for total time of 10 minutes.
- (6) Add sulfur on open mill.

carbon black-latex stocks were adjusted to give a final mix comparable in processing characteristics to that obtained when dry black was mixed with GR-S. Tables V and VI give the mixing recipes and mixing procedures for a 1000-pound batch in a Number 27 Banbury, with a rotor speed of 20 r.p.m.

It should be noted that the latex-black samples took only 10 minutes in the Banbury to reach satisfactory processing characteristics, compared to 17 minutes for conventional mixing. This represents a saving of about 40 per cent in processing time. It was noted also that the Banbury temperatures of the latex-black stocks were considerably lower than those of the controls. Comparative operating temperature curves are shown in Figure 1.

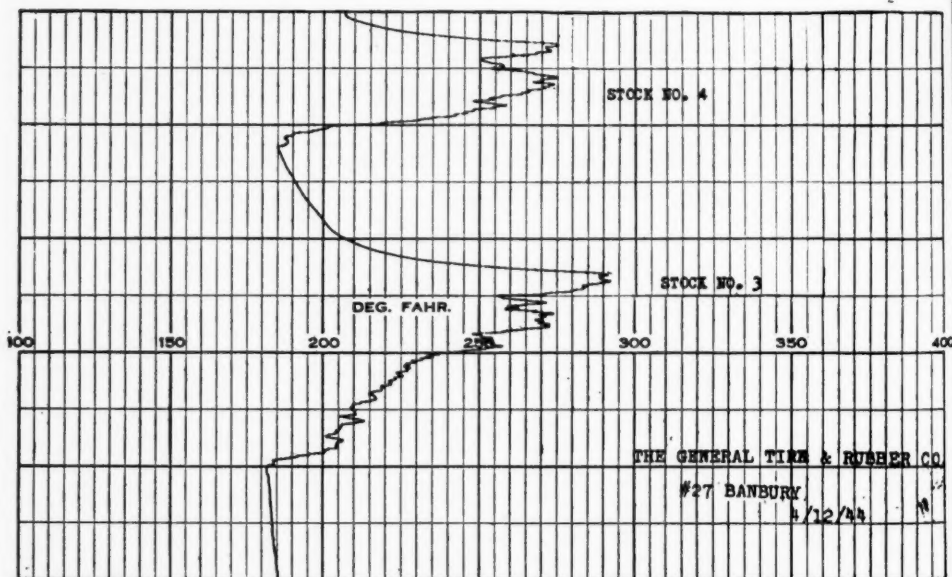
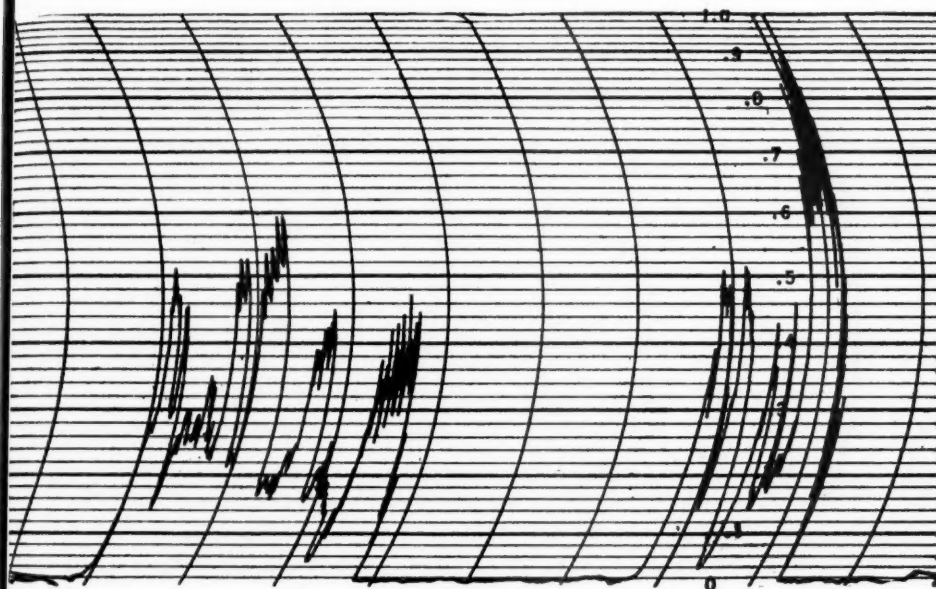


Fig. 1.—Comparative operating temperature curves.

A Number 11 Banbury was used to study the comparative power requirements for mixing batches of black-latex rubber compared with ordinary GR-S mixed with dry black. In this size equipment a 400-pound batch of GR-S tread stock normally required 10 minutes for mixing, compared to 6 minutes for a black-latex stock. The power consumption during mixing was measured by means of a recording power meter installed in the motor circuit. Average power requirements, total work, and peak loads were estimated from the resulting charts. Typical power data are shown in Figures 2 and 3.



Stock No. 1 (GR-S Control)
305 H.P. (Average)—44.8 K.W.H.
\$0.358

Stock No. 2
312 H.P. (Average)—26.2 K.W.H.
\$0.210

FIG. 2.—Power consumption—No. 11 Banbury—W-6 type mixing.

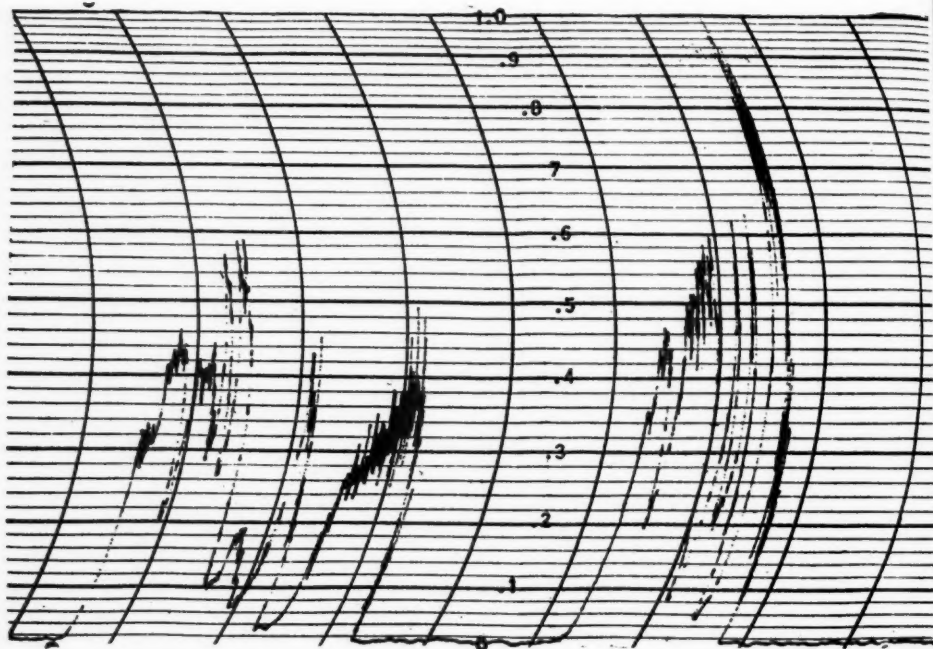
In general, the power charts show that the latex-mixed stocks require more power on the average and at the peak load than does the control, but that in spite of these larger requirements the total power consumption per batch is at least 20 per cent less for the black-latex stocks than for the direct mix. This saving is, of course, a reflection of the greatly decreased mixing time.

Tubing and other processing characteristics of the black-latex stocks were at least as good in every way as the controls. Tire building operations were normal, and no difficulties were experienced in building test tires.

Physical tests on both factory and laboratory mixes of these black-latex stocks show that they are comparable in every respect to GR-S, and may actually possess some advantages over GR-S into which dry black has been mixed. Typical comparative results of conventional factory-mixed stocks with black-latex stocks are shown in Table VII. These figures show that the latex mixed samples tend to have lower modulus, with higher tensiles and elonga-

tions. These findings have been confirmed in other laboratories, and represent what would be expected from better dispersion.

From road tests on 6.00×16 passenger tires run for approximately 17,000 miles at 60 miles per hour, the latex-mixed tires were rated slightly better in regard to tread wear than the control, and equal in crack resistance. This means that these special tires are at least comparable in all respects with tires made from standard GR-S mixed in the conventional way.



Stock No. 3 (GR-S Control)
260 H.P. (Average)—37.5 K.W.H.
\$0.300

Stock No. 4
385 H.P. (Average)—29.9 K.W.H.
\$0.239

FIG. 3.—Power consumption—No. 11 Banbury—Statex-93 type mixing.

PLANT CONVERSION

The excellent results of the quality and processing tests on these first factory scale runs induced Government permission to convert to commercial practice one-fourth of the 30,000-ton Government plant operated by the General Tire & Rubber Company at Baytown, Texas. The desirability of handling carbon black in bead form is obvious from a production and economy standpoint. The production installation was made on the basis of handling the black in bead form. Disintegration of the beads was accomplished by the use of an impact pulverizer manufactured by the Pulverizing Machinery Company. Although it was first believed necessary to pulverize the beads while dry, it was found preferable to make a wet disintegration of them in one step, which simplified the whole slurry preparation. The other steps are carried on essentially the same as made in the first plant run.

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TABLE VII
TYPICAL COMPARATIVE RESULTS OF CONVENTIONAL FACTORY-MIXED STOCKS WITH BLACK-LATEX STOCKS

	Stock No. 1				Stock No. 2				Stock No. 3				Stock No. 4			
	25	50	75	90	25	50	75	90	25	50	75	90	25	50	75	90
Cures at 287° F (minutes)																
Tensile strength	1290	2000	2340	2340	<i>Original (tested at room temperature)</i>				605	2110	2115	2000	605	2110	2115	2000
Elongation (percentage)	915	680	655	610	1055	2485	2655	2780	2215	2205	2060	570	855	730	620	570
Modulus at 300% elongation	180	505	630	715	1050	815	780	750	755	645	525	1030	120	580	820	880
Tensile strength	490	550	545	560	<i>Original (tested at room temperature)</i>				175	800	785	775	175	800	785	775
Elongation (percentage)	545	360	300	250	515	635	750	685	490	755	725	810	550	420	310	310
Modulus at 300% elongation	145	405	695	485	425	395	410	320	260	...	55	535	755	715
					121	270	430	500	315	660
					<i>Oven-aged 48 hours at 100° C</i>				1970	...	1600	...	1795	1750
Tensile strength	1910	2000	2310	2045	2950	2780	2375	2655	1650	1990	2030	1795	1845	1810	1970	1940
Elongation (percentage)	380	375	420	380	485	510	460	510	250	280	310	290	340	285	320	320
Modulus at 300% elongation	1310	1390	1410	1385	1225	1340	1355	1275	1600	...	1795	1750
					<i>Oven-aged (tested at 100° C)</i>			
Tensile strength	535	605	655	755	750	690	830	745	670	620	760	705	465	655	625	670
Elongation (percentage)	145	165	170	165	230	215	230	225	140	120	125	130	130	125	125	125
Mooney on compounded stock (4 min. reading)																
St. Joe Flexometer																
Cure at 287° F (minutes)																
Final temp. (° F)																
Goodrich Flexometer																
Cure at 287° F (minutes)																
Vertical load 175 lbs., 0.175 in. (minutes)																
Final temp. (° F)																
Goodyear-Healy rebound																
Cure (minutes)																
Rebound																
DeMattia flex-cracking																
Cure (minutes)																
Cycles																
Percentage cut growth at room temperature																

CONCLUSIONS

1. A commercially feasible method for adding carbon black to latex has been developed and tested. The black-latex mixture can be handled in essentially the same way as normal GR-S throughout the various steps of coagulation, washing, drying and baling.
2. By incorporating black into GR-S latex, an increase in milling capacity of about 35 per cent is possible.
3. The total power required for mixing this black-rubber is at least 20 per cent less than for tread stock mixed in the conventional way.
4. Mixing temperatures are lower for latex-black stocks.
5. Physical properties and preliminary tire tests show that carbon black incorporated with the latex produces stock equivalent in physical properties to stocks prepared by mixing carbon black into dry rubber.
6. Considerable savings are made possible by the use of this method.
7. The amount of dirt now present in the millrooms of the rubber manufacturing plants should be greatly reduced.

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We are grateful for the helpful suggestions and constructive criticisms of L. J. Venuto, of the Binney & Smith Co., and H. F. O'Connor, of the Research Department of the Columbian Carbon Co. William Sheldon, of the Pulverizing Machinery Co., also gave unstintingly of his knowledge and experience. Without the coöperation of J. H. Faull and J. Keith, and their respective technical and engineering staffs, the plant scale production would have been impossible. Finally, the authors wish to thank J. C. Butler, Guy Reymond and Robert Baker, of the research staff of the General Tire & Rubber Co., for their help in the preparation of this article.

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- ¹ Among the more important patents are U. S. patents 1,610,226; 1,611,278; 1,802,761; 1,802,764; 1,807,355; 1,822,548; 1,862,270; British patents 250,279; 273,961; 282,011; 368,256; French patents 679,992; 697,568; 700,533. Among the more important publications are McMahon and Kemp, *Ind. Eng. Chem.* **36**, 375 (1944); O'Connor and Sweitzer, *Rubber Age* (N. Y.) **54**, 424 (1944).
- ² O'Connor and Sweitzer, *Rubber Age* (N. Y.) **54**, 424 (1944).

EFFECT OF MOISTURE ON CURING RATE OF GR-S*

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One of the most serious variables in GR-S has been its curing rate. This is illustrated in Figure 1, where two shipments of standard GR-S are compared. The base mixture was: GR-S 100, EPC black 50, coal tar softener 5, zinc oxide 5, mercaptobenzothiazole 1.5, sulfur 2. It might be argued that the variations shown in curing rate are no greater than those which sometimes occur with Hevea, but curative setups which were developed for natural products were remarkably flat with respect to time of curing. Because of this and the

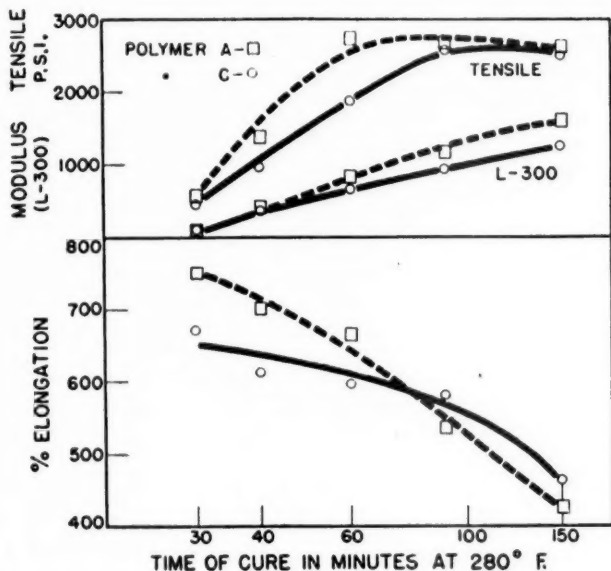


Fig. 1.—Cure variations in polymers.

relatively excellent heat stability of Hevea, there was a general tendency, particularly in tires, to cure "tight". Such a practice cannot be directly transferred to GR-S compounds. Some accelerators do give remarkably flat tensile and modulus curves as cure is increased, but flex cut-growth resistance still remains abnormally sensitive to overcure and to heat aging. Production cures must, therefore, be more closely controlled than was necessary with Hevea.

The selection of comparable states of cure in GR-S is still far from an exact

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science. Any system based on modulus is liable to confusion if normal variations exist in the gel content of the polymer as manufactured, as well as in the time and particularly the temperature of processing, to mention only two causes of modulus fluctuation not attributable to cure alone. Therefore this laboratory has continued to select cures by hand for the best balance between snap and tear.

Moisture affected the curing rate of Hevea, and now it is also known to affect the cure of GR-S accelerated with thiols. In GR-S the problem is more serious because of the need of closer control of cure. The order of moisture content which affects cure is illustrated in Figure 2, which covers tests, in the

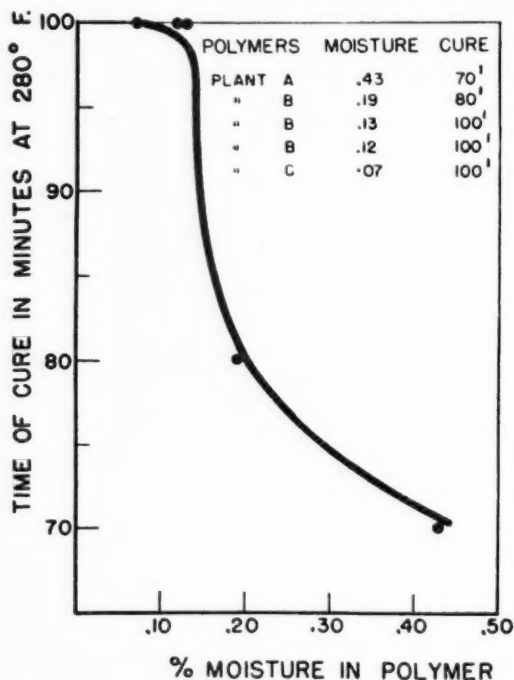


Fig. 2.—Effect of polymer moisture on curing rate of GR-S.

basic compound given above, of five shipments of polymer from three different sources.

It appears that at about 0.15 per cent moisture there is a sharp break in the effect of moisture on cure. The futility of setting a minimum moisture specification on a material which may contain traces of a hygroscopic soap is apparent.

CARBON BLACK AS SOURCE OF MOISTURE

Most GR-S compounds require carbon reinforcement; in tread compounds particularly, carbon blacks are by far the largest volume addition to GR-S. They may vary in moisture content by more than the equivalent of the 0.15 per cent shown as the breaking point in the curve of Figure 2. Rubber-grade channel carbon exposed to 100 per cent relative humidity at room tem-

perature can pick up a maximum of 4 per cent moisture (Figure 3). It was thus natural to suspect possible variations in moisture content of carbon black as contributing to cure variation. At the request of the Office of Rubber Director, the Carbon Black Nomenclature Committee investigated the effect of moisture in carbon black on the curing rate of GR-S. The results are summarized graphically in Figure 4. The normal moisture content of com-

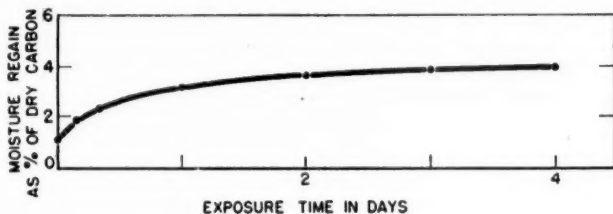


FIG. 3.—Moisture regain in rubber channel-carbon over water.

mercial rubber carbons, as delivered to the rubber manufacturer, varies between about 1 and 3 per cent. The maximum content by absorption during shipping and storage is about 3 per cent. The bone-dry sample of Figure 4 was artificially dried to 0.05 per cent moisture and added to the mix directly from the drying oven. Samples were conditioned over water to various moisture contents up to 3.5 per cent. For moisture contents in excess of this amount, it was necessary to add water to the carbon immediately before

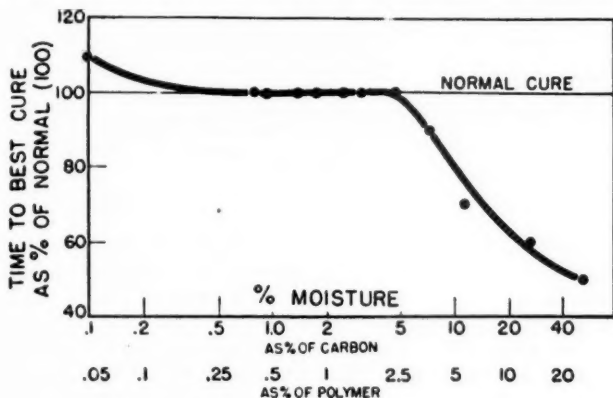


FIG. 4.—Effect of moisture in carbon black on cure of GR-S.

mixing. Apparently the normally occurring amounts of moisture on carbon black are held so tightly that they do not affect cure. The absorptive power of bone-dry black is shown to be so great as to dehydrate the polymer itself and retard its cure. Moisture present in excess of the absorptive capacity of the carbon has a sharp accelerating effect, roughly proportional to the amount of water added.

SOAP AND WATER-SOLUBLE SALTS

It was thought that this cure variation might be due to residual soaps in the polymer or to water-soluble salts remaining because of insufficient washing

after coagulation; various expedients (Table I) were tried to determine this in the 50 per cent EPC tread base. One per cent. of soap (Ivory Flakes) was added to the polymer on the mill, with no effect on rate of cure. The same amount of soap with 5 per cent of water on the polymer gave a 30 per cent increase in rate of cure. The addition of 5 per cent water without the soap gave the identical 30 per cent increase in rate of cure.

With the idea that soluble sulfates might be present, a channel carbon produced with a pH of 7 (Hi-tear Micronex) was substituted for EPC; a 10 per cent increase in rate of cure resulted, an effect to be expected wholly from the increase in pH of the carbon. The same carbon with added water gave a 50 per cent increase in curing rate, as did standard EPC carbon with added water. To be doubly sure that any possible sulfates might be neutralized, a dilute solution of sodium hydroxide was added to EPC before its incorporation into the GR-S; there was a 60 per cent increase in curing rate. This gave distinct evidence that water, rather than traces of sulfates or other electrolytes, was the determining factor in curing rate.

TABLE I

EFFECT OF SOAP AND WATER-SOLUBLE SALTS ON VARIATION IN CURE OF GR-S (50 PER CENT EPC TREAD BASE)

Variables	Cure effect
1% soap (Ivory Flakes) added	No effect
1% soap + 5% water added	30% increase
5% water added	30% increase
Hi-tear Micronex (pH 7) substituted for EPC	10% increase
Hi-tear Micronex + 5% water added	50% increase
EPC + 5% water added	50% increase
EPC + 5% dilute NaOH solution	60% increase
Slow-curing polymer (0.08% water), ORD Survey 17	Control
5% water added	45% increase
Polymer preconditioned over water to 2% moisture	60% increase
Polymer soaked in water to 4% moisture	75% increase
Polymer washed and redried	No effect

This laboratory was also invited to participate in the investigation of a sample of slow-curing polymer (ORD Survey No. 17) which had required recompounding to correct its slow cure. This polymer was found to be excessively dry (0.012 to 0.08 per cent moisture). Addition of 5 per cent water (on the polymer) with the carbon in the test compound speeded the cure 45 per cent; conditioning the polymer over water to a 2 per cent moisture content speeded the cure 60 per cent; raising the moisture content of the polymer to 4 per cent by soaking it for several days in water speeded its cure 75 per cent. Another participant (American Cyanamid Company) in this investigation washed the polymer and found chloride and sulfate ions in the wash water, but after drying to the original moisture content there was no increase in rate of cure.

These tests seemed to indicate (without revealing the mechanism) that moisture content is the determining factor in the rate of cure of GR-S accelerated with thiols.

CONDITIONING OF MIXED STOCKS

In RRC-ORD Survey No. 18, the effect of moisture as varied through conditioning of a mixed tread stock was investigated. The basic GR-S tread

compound was formulated with three polymers (Figure 5) and conditioned as milled sheet, under 0, 60, and 100 per cent relative humidity for periods up to 2 weeks. Three cures, 25, 50, and 90 minutes at 292° F, were given. A modulus of 1000 pounds per square inch at 300 per cent elongation was selected as the criterion of comparable cure, and the times to this cure were plotted against moisture content of the milled sheet. This use of modulus was justifiable, since all sheets of each base polymer were from a single blend of laboratory-mixed stocks with no reprocessing after conditioning. Examination of Figure 5 suggests the following: (1) the accelerating effect of moisture is confirmed; (2) the wide variability in curing rate of any single polymer and of all three polymers when moisture content lies below 0.5 per cent (on the mixed stock) is evident; (3) moisture contents below 0.25 per cent (of mixed stock) not only do not guarantee uniform curing rate but are difficult to ensure in factory production, and (4) there is an indication that, between 0.5 and 1 per

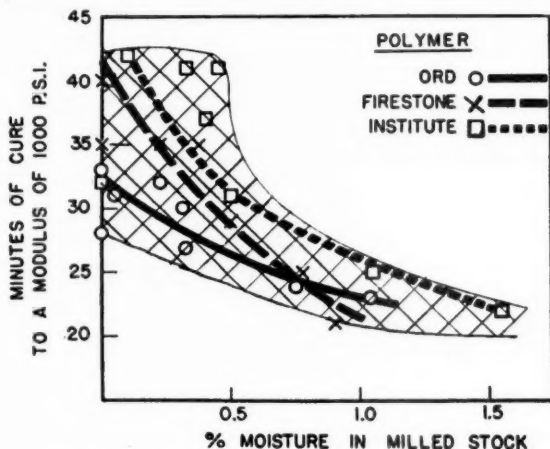


FIG. 5.—Effect of moisture on curing rate of GR-S.

cent moisture (on the mixed stock), the variability in curing rate between polymers is substantially ironed out.

STABILIZATION OF CURING RATE OF GR-S

The moisture control of raw GR-S at the plants to within the limits indicated as desirable is presumably not practical. Drying the polymer to very low moisture is no guarantee of its moisture content when compounded since, according to ORD Survey No. 18, raw polymer with even a trace of soap can pick up well over 2 per cent of moisture in a saturated atmosphere within 2 weeks (Figure 6).

Conditioning of mixed stocks to a moisture content of 0.5 to 1.0 per cent, which is indicated as desirable for stable cure by Figure 5, is, in general, not feasible in production. The question of deliberate moisture addition has, therefore, been investigated. No dry polymer (less than 0.15 per cent water) was available, but the polymer from plant B with 0.19 per cent water (Figure 2) was selected. The test compound employed was: GR-S 100, EPC 50, coal-tar softener 7.5, zinc oxide 3, benzothiazyl sulfenamide 1.2, sulfur 1.8, water 0, 2.5, 5, 10, and 20.

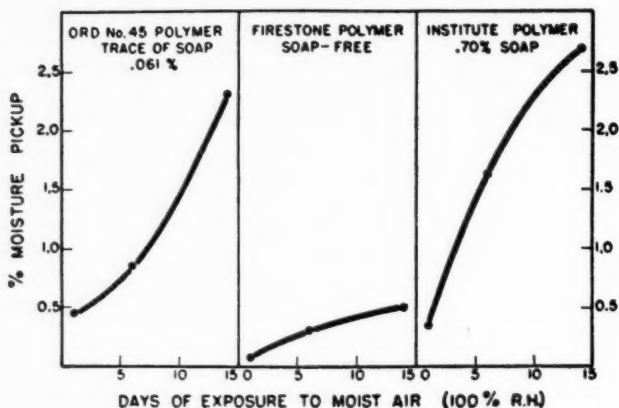


FIG. 6.—Moisture pickup by raw GR-S.

Water was stirred into the carbon black beads immediately before mixing. By using the higher ratios, it was felt that sufficient moisture would be retained to cause blowing troubles under factory curing conditions. Mill roll temperatures were kept at 120° F, and stock temperature ran 20° to 30° higher. This temperature is admittedly cool compared with factory mixings, but the ratio of surface exposed per pound of stock processed and time of exposure are also much higher, and thus compensate in part for the lower temperature.

Stocks were mixed in 20 minutes, rested 16 hours, remilled, and then sheeted out in 4 minutes. Moisture determinations were made after this resheeting. Stocks were cured within 16 hours of resheeting. Moisture in mixed stock was determined by oven drying of the laboratory-sheeted stock for 24 hours at 150° F. Allowance was made for the evaporation of coal-tar softener, since

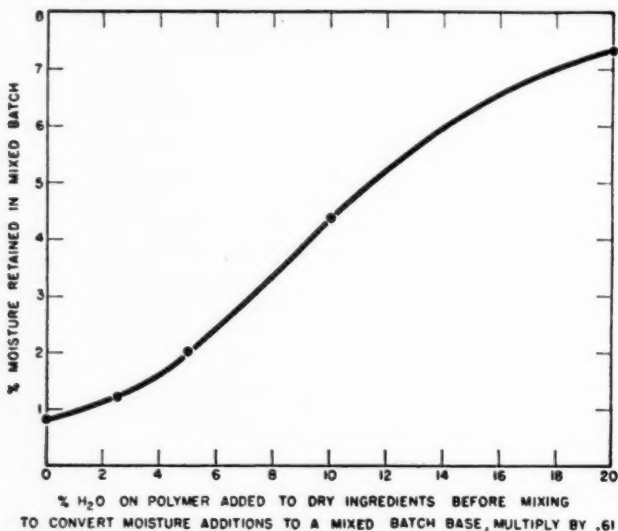


FIG. 7.—Moisture retention of a GR-S tread stock mixed on a laboratory mill.

the particular sample lost 9.25 per cent of its weight when exposed under these drying conditions.

The moisture retention is illustrated in Figure 7. The samples to which 10 and 20 per cent of water (on the polymer) had been added and which retained 4.4 and 7.3 per cent of moisture (on the mixed stock) showed water stains in the curing molds. The samples to which 2.5 and 5 per cent water

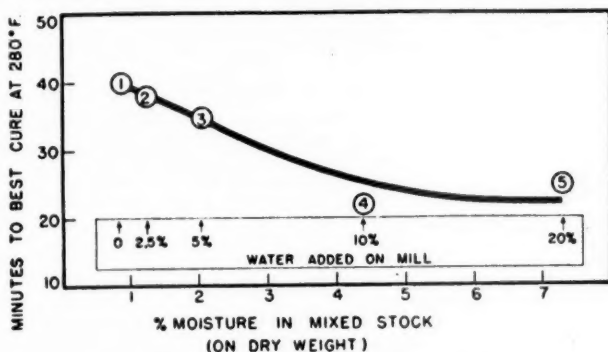


Fig. 8.—Effect of moisture on curing rate of GR-S tread.

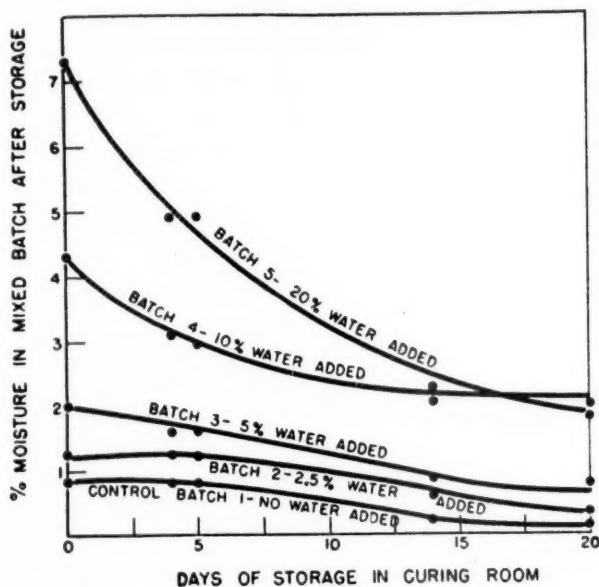


Fig. 9.—Effect of storage on moisture content of GR-S tread.

(on the polymer) had been added and which retained 0.83 and 1.24 per cent moisture (on the mixed stock), respectively, gave no trouble in curing.

The curing times to best cure are shown in Figure 8. The first sample with no water added was already out of the slow-curing zone, as judged by moisture content of the polymer (Figure 2) and by moisture content of the mixed stock (Figure 5). The extra water in the second and third samples

produced only a 5-minute increase in rate of cure, *i.e.*, within the range of cure variation shown for the three polymers of Figure 5, when conditioned to 1 per cent moisture. The extra moisture retained by the batch to which 5 per cent water on the polymer was added would also be sufficient to avoid slow cure, if excessively dry polymer had been employed. Samples 4 and 5, with 10 and 20 per cent water on the polymer added, showed marked cure acceleration confirming the trend in Figure 4.

EFFECT OF STORAGE

Samples of the same five mixings were left exposed in the vulcanizing room of the laboratory for 3 weeks, and the change in moisture content on storage was determined. During that time, temperature fluctuated between 84° and 50° F, with an average of 73° F. Relative humidity ranged from 65 to 40 per cent, with an average of 47 per cent, in short, about average factory conditions.

The drift in moisture content on storage of the five stocks is shown in Figure 9. (1) All stocks lost moisture. (2) The control stock in 3 weeks reached a low moisture level (0.19 per cent), where slow and erratic curing rate might be expected according to Figure 5. (3) Up to 3-week storage, either of the next two stocks (2.5 and 5 per cent water added) could be expected to vary but slightly in curing rate. (4) The stocks with the higher amounts of added water (10 and 20 per cent) even after 2 weeks contained undesirably and unnecessarily large amounts of moisture.

CONCLUSIONS AND RECOMMENDATIONS

1. Moisture content of uncured GR-S compounds must be reckoned with because of its effect on curing rate and the serious consequence of overcure.

2. Excessively dry polymer (below about 0.15 per cent water) will, in general, be slow curing (Figure 2).

3. Mixed stock with less than 0.5 per cent water will, in general, be slow curing and erratic in curing rate (Figure 5).

4. The normal moisture range of carbon black does not affect the curing rate of GR-S (Figure 4).

5. The normal moisture content of carbon black is not available to the polymer for stabilizing its curing rate.

6. Mixed stock which is dry and slow curing may be conditioned to stable curing rate by storage under humid conditions. A moisture content of 0.5 to 1.0 per cent is indicated. This moisture content seems also to iron out differences in curing rate between polymers.

7. Since conditioning of mixed stocks is not always feasible on the factory scale, the stabilization of cure by direct water addition during mixing should be given consideration.

8. Laboratory-scale tests on a GR-S tread compound indicate that an addition of about 2.5 to 5 per cent water (on the polymer) during mixing will result in a mixed-stock moisture content giving minimal cure variation for normal-curing and slow-curing (very dry) polymers for periods of stock layover up to about 3 weeks.

9. Any additions of water as suggested above will, on the factory scale, require adjustment, since moisture retention is a function of the compounding ingredients, mixing cycle and temperature, storage time, and humidity conditions actually obtaining.

EFFECT OF ELASTOMER CRYSTALLIZATION ON TESTS FOR FREEZE RESISTANCE *

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At subzero temperatures cured elastomers become stiff and may or may not become brittle. As stiffness increases, elasticity decreases and stress at any given elongation increases. Brittleness occurs when the elastomer reaches an inelastic state. Both time and temperature of exposure are important factors which affect these changes in properties. Under any given testing methods, the degree of stiffness and conditions of brittleness are intrinsic properties of the elastomers and their compounds. Summaries of these factors have been given by Liska¹ and Graves and Davis².

Crystallization, which explains some of the results to be described, has been known for a long time to occur in rubber. Factors influencing the crystallization of rubber were investigated by Bekkedahl³. He concludes that the crystals formed during the freezing or the stretching of rubber are identical. It is believed that this is true for crystallizable elastomers.

Carothers and coworkers⁴ and later Sebrell and Dinsmore⁵ reported that the x-ray pattern of Neoprene (polychlorobutadiene) crystals obtained on stretching resembles those of rubber. Wood⁶ showed that Neoprene, like rubber, crystallizes at low temperatures. The most favorable temperature for Neoprene Type GM appears to be 0° C, and Neoprene Type FR shows no crystallization at low temperatures. Some properties of the latter at low temperatures were reported by Yerzley and Fraser⁷.

Although considerable information on the properties of elastomers at low temperatures has been reported, few of the investigators have considered the possible effects of time of exposure. It was decided to study the changes that occur during long exposures at -17.8°, -28.9°, and -40° C (0°, -20°, and -40° F). Rubber, GR-S, Neoprene Type FR and Neoprene Type GN were selected, and the stiffening of their compounds was followed by observing changes in hardness.

The results show striking similarities between rubber and Neoprene Type GN and also between GR-S and Neoprene Type FR. Accordingly, the two Neoprenes were selected for a more extensive study that included the effects of plasticizers on these polymers. This had the added advantage of providing data for the classification of the plasticizers for improving the freeze resistance of Neoprene compounds.

Table I gives the formulas of the compounds studied. The stiffening of these stocks was measured with the apparatus described by Yerzley and Fraser⁷. Readings were made after approximately 15 seconds, which corresponds to the suggestions of Taylor⁸ for using the Shore durometer. The measurements were made at various times during long exposures to a given

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TABLE I
 FORMULAS FOR ELASTOMER COMPOSITIONS

Compound	A	B	C	D	E	F	G	H	K
Neoprene Type GN	100	100	100	100
Neoprene Type FR	100	100	100
Rubber (smoked sheet)	100	...
GR-S	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	...
Neozone A ^a	2	2	2	2	2	2	2	1	...
Extra-light calcined magnesia	4	4	4	4	5	5	5
MT black	...	57.6	57.6	57.6	62	62	62	77.4	77.4
Plasticizers	15	30	...	15	30
Zinc oxide	5	5	5	5	5	5	5	5	5
Permalux ^b	1	1	1
Sulfur	2	2
Accelerator 2-MT ^c	0.75	0.75
Accelerator 808 ^d	0.15	0.15

^a Phenyl- α -naphthylamine^b Di- α -tolylguanidine salt of decatechol borate^c 2-Mercaptothiazoline^d Butyraldehydeaniline condensation product

temperature or after short exposures to progressively lower temperatures. Brittleness tests were made by the methods of Martin⁹ and Bimmerman and Keen¹⁰ so that comparisons of stiffness with brittleness would be available. The viscosity measurements on the plasticizers were made in an Ostwald viscometer¹¹ immersed in a circulating coolant.

STIFFENING OF ELASTOMERS

To compare the stiffening of rubber, GR-S, Neoprene Type GN, and Neoprene Type FR, compounds B, E, H, and K (Table I) were prepared. Physical properties are shown in Table II.

 TABLE II
 STRESS-STRAIN PROPERTIES OF GR-S NEOPRENE AND RUBBER STOCKS

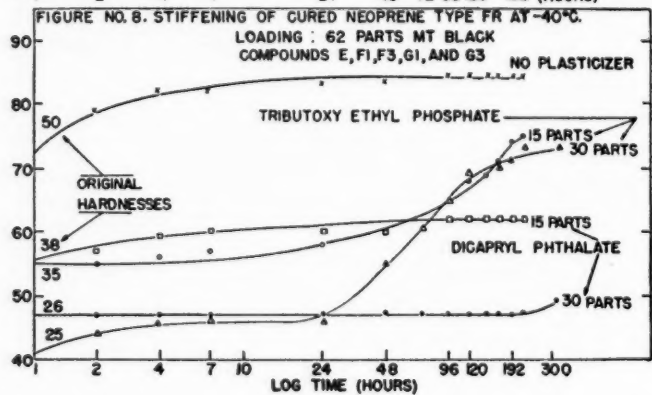
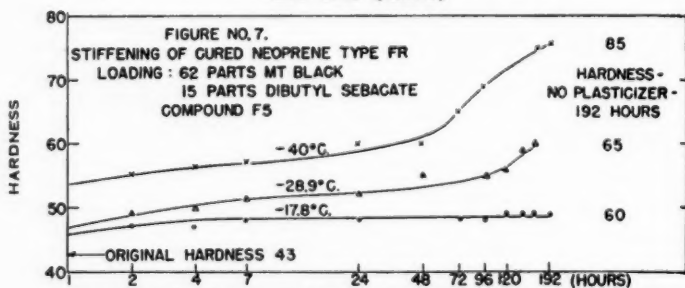
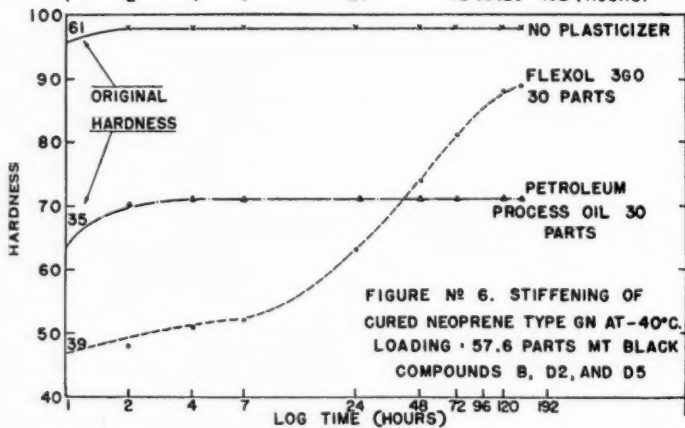
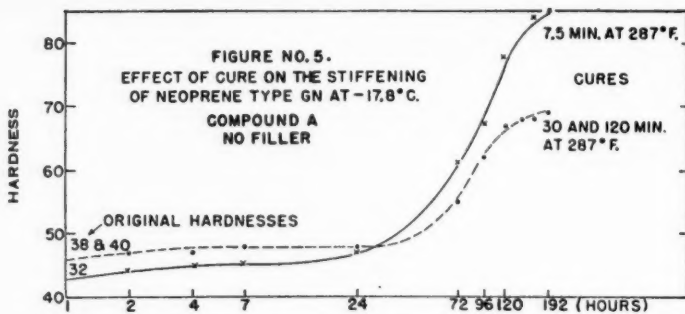
Compound	B	E	K	H
Elastomer	Neoprene-GN	Neoprene-FR	GR-S	Rubber
Cure (min. (° C))	30 (142)	30 (142)	90 (138)	45 (138)
Stress at 300% (lbs. per sq. in.)	1050	825	...	1475
Tensile (lbs. per sq. in.)	1675	1275	1700	3400
Elongation at break (%)	600	510	270	570
Hardness	57	52	61	56

Hardness measurements were made on these compounds during short exposures to progressively lower temperatures. The results (Figure 1) show that all of the elastomers eventually attain the same general degree of stiffness, and that the order of stiffening rates is Neoprene Type GN, Neoprene Type FR, GR-S, and rubber. This same order was also noted at the end of 1-hour exposure to temperatures of -17.8° , -28.9° , and -40° C.

The same vulcanizates (B, E, K, and H) were exposed for approximately 200 hours at -17.8° , -28.9° , and -40° C. The observed increases in hardness shown in Figures 2, 3, and 4 varied considerably during the tests. At each temperature the elastomers appeared to reach an equilibrium degree of stiffening in 2 to 4 hours. However, large changes were later observed for rubber at each temperature and for Neoprene Type GN at -17.8° C. These delayed increases in stiffness generally began after approximately 48 hours and continued for several days. In these tests both Neoprene Type GN and

Figure No. 4 is a line graph titled "STIFFENING OF CURED ELASTOMERS AT -40°C . COMPOUNDS B, E, H, AND K". The Y-axis is labeled "HARDNESS" and ranges from 50 to 100. The X-axis is labeled "LOG TIME (HOURS)" and ranges from 1 to 192. The graph shows the change in hardness over time for five different elastomer samples. The "ORIGINAL HARDNESSES" are indicated by horizontal lines at the top of the graph. The "NEOPRENE TYPE GN" and "NEOPRENE TYPE FR" curves show a sharp increase in hardness after 48 hours, reaching a plateau around 86. The "RUBBER" and "GR-S" curves show a more gradual increase, reaching a plateau around 72. The "ORIGINAL HARDNESSES" curve remains relatively flat, indicating no significant change in hardness over time.

Log Time (Hours)	ORIGINAL HARDNESSES	NEOPRENE TYPE GN	NEOPRENE TYPE FR	RUBBER	GR-S
1	95	95	72	72	72
2	95	95	82	72	72
4	95	95	84	72	72
7	95	95	85	72	72
24	95	95	85	72	72
48	95	95	85	72	72
72	95	95	85	72	72
96	95	95	85	72	72
120	95	95	85	72	72
192	95	95	86	72	72



rubber were approaching a new hardness level after 200-hour exposure. These changes in the hardness of Neoprene Type GN as measured with the Shore durometer are in close agreement with the changes in Young's modulus with time as reported by Liska¹.

Investigation of the literature¹² indicated that this effect was probably due to crystallization. Although the optimum temperatures (0° C for Neoprene Type GN and -22° C for rubber) were not represented, those used were within the crystallization range. Accordingly, Neoprene Type GN (crystallizable) and Neoprene Type FR (noncrystallizable) were selected for more detailed investigation.

NEOPRENE-GN, CRYSTALLIZABLE ELASTOMER

The crystallization of a Neoprene Type GN gum vulcanizate (compound A) is illustrated in Figure 5. The time at which crystallization began to accelerate was commensurate with that of the loaded compound in Figure 2. However, the increase in stiffness of the gum stock was much greater. It was subsequently observed that the magnitude of this increase in stiffness due to crystallization is inversely proportional to loading by filler. Figure 5 further shows that an extension of cure both delays the start and limits the extent of crystallization as measured by increased hardness. It appears that the effects of extended cure are shown only in the early stages of cure, since the results obtained on the 30- and 120-minute cures were identical.

Preliminary experiments indicated that, during exposure at -17.8° C, compounds containing dibutyl sebacate appeared to undergo the characteristic hardness increase due to crystallization. The effects of plasticizer on crystallization were not apparent from these results. Therefore a series of experiments was run at -40° C with Neoprene Type GN stocks containing different plasticizers. This temperature was selected because it has been shown to be too low for crystallization of neoprene compounds not containing plasticizers.

The results obtained with several plasticizers are summarized in Table III. The curves in Figure 6 represent the observed effects. At -40° C the control stock (compound B) rapidly stiffened to a high level, the Flexol-3GO stock (D-2) showed the delayed increase in hardness, and the petroleum process oil stock (D-5) reached an intermediate level that was maintained throughout the test. There are two possible explanations for the delayed stiffening of the Flexol-3GO compound—depressed crystallization point of the elastomer, and incompatibility of softener. The latter theory appears to be more acceptable, since noncrystallizable Neoprene Type FR compounds containing softener show the same effects.

The stress-strain properties of plasticized Neoprene Type GN compounds are also shown in Table III.

NEOPRENE-FR, NONCRYSTALLIZABLE ELASTOMER

The most interesting observation during the investigation of Neoprene Type FR compounds was the delayed stiffening of those containing plasticizers. The curves in Figure 7 on compound F-5 containing 15 parts dibutyl sebacate show no delayed stiffening at -17.8° C, but it was observed at both -28.9° and -40° C. The magnitude of the effect was greater at the lower temperature. This appears to indicate plasticizer incompatibility at the lower temperatures. In Figure 8 the curves show compatibility for dicapryl phthalate and incompatibility for tributoxymethyl phosphate. It should be noted that

TABLE III
PROPERTIES OF PLASTICIZED NEOPRENE COMPOUNDS

Com- pound ^a	Plasticizer, parts	Stress-strain properties			Relative stiffening as hardness after exposure at -40° C for				
		Stress at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elonga- tion (%)	Shore hardness	1.58 ^b hrs.	24 hrs.	120 hrs.	200 hrs.
Neoprene Type GN Compounds									
A	None (gum)	175	3450	995	38	90	93	93	93
B	None (MT black)	1050	1650	540	61	85	98	98	98
C-1	Dibutyl sebacate, 15	600	1625	770	44	61	61	78	81
C-2	Tributoxyethyl phosphate, 15	550	1750	640	45	66	69	75	78
D-1	Tributoxyethyl phosphate, 30	350	1550	655	36	46	56	89	91
D-2	Flexol-3GO, ^c 30	450	1600	820	39	48	60	86	91
D-3	Tricresyl phosphate, 30	400	1575	730	40	85	100	100	100
D-4	Dicapryl phthalate, 30	450	1650	800	44	51	54	57	64
D-5	Petroleum process oil, ^d 30	450	1825	875	35	49	71	71	71
Neoprene Type FR Compounds									
E	None	850	1250	485	50	72	82	84	84
F-1	Tributoxyethyl phosphate, 15	325	1300	975	35	56	58	68	75
F-2	Flexol-3GO, ^c 15	475	1250	940	39	55	57	65	71
F-3	Dicapryl phthalate, 15	350	1250	980	38	55	60	62	62
F-4	Tricresyl phosphate, 15	450	1650	1010	40	65	76	78	78
F-5	Dibutyl sebacate, 15	400	1300	1100	43
G-1	Tributoxyethyl phosphate, 30	125	1225	1160	25	42	46	69	73
G-2	Flexol-3GO, ^c 30	225	1125	1095	27	40	51	60	73
G-3	Dicapryl phthalate, 30	225	1100	1075	26	43	47	47	48
G-5	Dibutyl sebacate, 30	250	1075	1055	27	41	77	81	89
G-6	Dibenzyl ether, 30	275	1350	1050	30	39	49	55	65

^a All stocks cured 40 min. at 153° C, except those of compound A cured 30 min. at 142° C; C and D series based on compound B; F and G series based on compound E.

^b Exposed to progressively lower temperatures down to -40° C (Figure 1 gives time cycle).

^c Triethylene glycol di-2-ethyl hexoate.

^d Circo process oil.

the two compounds containing the latter softener approach the same ultimate degree of stiffness. The stress-strain properties and the low-temperature stiffening of the Neoprene Type FR compounds studied are summarized in Table III.

BRITTLENESS

None of the compounds exposed to -40°C for 200 hours became brittle in the Martin apparatus⁵. When the compounds were tested once daily during 72-hour exposure to -54°C , all of the Neoprene stocks containing 15 parts of softener became brittle before the end of the experiment. With 30 parts of softener, the Neoprene Type GN compound (Flexol-3GO) and all of the Neoprene Type FR stocks were flexible after 72 hours.

Brittle points were also determined after short exposures to low temperatures. The results obtained by a slight modification of A.S.T.M. Designation D736-43T⁵ are generally lower than those obtained by the method of Bimmerman and Keen¹⁰.

Data on the brittleness tests are compiled in Table IV. The results indicate that this property of elastomers is independent of crystallization, and

TABLE IV
BRITTLENESS OF COMPOUNDS INVESTIGATED

Elastomer	Compound	Plasticizer, parts	Method of test		
			Bent loop ⁸		Solenoid ¹⁰ ($^{\circ}\text{C}$)
			Temp. ($^{\circ}\text{C}$)	Days at -54°C	
Neoprene type GN	A	None (gum)	-51
	B	None (gum)	-46	1	-40
	C-1	Dibutyl sebacate, 15	-62
	C-2	Tributoxyethyl phosphate, 15	-51	1	-43
	D-1	Tributoxyethyl phosphate, 30	-62	1	-48
	D-2	Flexol-3GO, 30	-62	>3	-54
	D-3	Tricresyl phosphate, 30	-57	1	-40
	D-4	Dicapryl phthalate, 30	-46	1	...
	D-5	Petroleum process oil, 30	-57	1	...
Neoprene type FR	E	None	-57	1	-45
	F-1	Tributoxyethyl phosphate, 15	-62	2	-60
	F-2	Flexol-3GO, 15	-62	2	-60
	F-3	Dicapryl phthalate, 15	-57	1	...
	F-4	Tricresyl phosphate, 15	-57	1	-45
	F-5	Dibutyl sebacate, 15
	G-1	Tributoxyethyl phosphate, 30	-68	>3	...
	G-2	Flexol-3GO, 30	-68	>3	-70
	G-3	Dicapryl phthalate, 30	-68	>3	...
	G-5	Dibutyl sebacate, 30	-68	>3	...
	G-6	Dibenzyl ether, 30	-68	>3	...
Rubber	H	None	-62
GR-S	K	None	Below -62

that it cannot be based on a measured degree of stiffness. The brittle point has been observed to be related to, but somewhat higher than, the temperature of second-order transition observed in all high-molecular-weight compounds having rubberlike properties. The second-order transition differs from a first-order transition, *e.g.*, crystallization, in that the transition is accompanied by

no change in volume and no exchange of latent heat. However, it is characterized by a definite change in the specific heat and in the coefficient of thermal expansion.

PLASTICIZERS

Modified Ostwald viscosities at different temperatures are shown in Table V. The data in Tables III, IV, and V are helpful in selecting plasticizers for freeze-

TABLE V
RELATIVE VISCOSITY OF PLASTICIZERS AT LOW TEMPERATURES

Plasticizer	Modified Ostwald Viscosity ¹¹ (seconds)					
	25° C	15° C	0° C	-10° C	-20° C	-40° C
Tributoxyethyl phosphate	29	41	90	168	306	> 1200
Flexol-3GO	37	60	131	275	692	> 1200
Tricresyl phosphate	233	980	> 1200	"
Dibenzyl ether	12	15	30	46	80	390
Dicapryl phthalate	124	270	918	> 1200	"	...
Dibutyl sebacate	21	31	55	89	Frozen	...
Petroleum process oil	200	450	> 1200	"

* Too viscous

resisting Neoprene compounds. The effectiveness of a plasticizer may be different in Neoprene Types FR and GN. The more viscous plasticizers appear to be more compatible on long exposures, but lower brittle points are obtainable with the most limpid plasticizers. All softeners should have low vapor pressures and high boiling points to prevent loss during processing at moderate heat service.

The data on plasticizers suggest that better freeze-resisting compositions could be made by the use of one or more softeners in the same compound. Many practical applications have already shown this to be true. Preliminary tests in this laboratory confirmed our belief that plasticizer blends should include a material that depresses the brittle point significantly, and a material that does not become incompatible with the elastomer after a long exposure to a freezing temperature.

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EFFECT OF ACCELERATORS ON THE HEAT EMBRITTLMENT OF GR-S VULCANIZATES *

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INTRODUCTION

Two of the most serious shortcomings of GR-S type synthetic rubber are its poor resilience, leading to excessive heat build-up under severe stress cycles, and its property of hardening during exposure to heat in service. Heat embrittlement aggravates heat build-up and vice-versa, so a vicious circle develops which eventually leads to failure. The problem of minimizing heat embrittlement has received considerable attention, and much work on the subject has been published. Some of this published work is reviewed briefly below, and an account is given of certain experiments carried out in this laboratory. The results of these experiments enable some preliminary conclusions to be drawn on one aspect of the problem, namely, the effect of accelerators on the heat embrittlement of GR-S.

PUBLISHED WORK

Shelton and Winn¹ noticed that the hardening effect observed on heating GR-S vulcanizates in a bomb at 80° C was independent of the presence of oxygen, and took place to an equal extent in the presence of nitrogen. On aging at 100° C, however, they observed that more than half the increase in modulus on heating could be attributed to the presence of oxygen. The conclusions of Sturgis, Baum and Vincent² are at variance with this latter result, since they reported that there was much hardening on heating the vulcanizates in nitrogen at 100° C as with oxygen. They observed further that the effect of accelerator activity on heat stability, *i.e.*, heat embrittlement resistance, was very slight, and that the effect of sulfur content was noticeable but not large. Nevertheless, they concluded that the system GR-S-sulfur was inherently unstable, and recommended sulfurless vulcanization, using dinitrobenzene as the vulcanizing agent. Neal and Ottenhoff³, using exclusively mercaptobenzothiazole-diphenylguanidine acceleration, claimed that high accelerator and low sulfur content tends to give good heat stability in GR-S vulcanizates.

Massie and Warner⁴ have observed that so-called persistent accelerators give a modulus which steadily increases with time of cure, while nonpersistent accelerators minimize this effect. Low sulfur formulations show better heat stability than more conventional stocks. Juve and Garvey⁵ have shown that the rate of sulfur combination with GR-S under vulcanizing conditions is faster and more complete with tetramethylthiuram monosulfide than with mercaptobenzothiazole-diphenylguanidine acceleration. They suggest that

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such "flat-curing" accelerators, because they promote more rapid and complete sulfur combination, do not leave so much free sulfur to cause embrittlement on heating. They noted that, with tetramethylthiuram monosulfide, overcures give better heat stability than undercures, although they did not observe this effect in the case of mercaptobenzothiazole-diphenylguanidine acceleration.

A more recent paper by Hendricks⁶ is of considerable interest, and to some extent sums up previous work. Hendricks points out that a compound designed to give good heat build-up, *i.e.*, a compound with fairly high proportions of sulfur and accelerator, tends to show poor heat stability, while a compound with low sulfur content, designed to give good heat stability, tends to give high heat build-up on stressing. He suggests that the most satisfactory compromise, to get satisfactory heat stability and heat build-up, comes from vulcanizing GR-S with a minimum of sulfur "driven home" by a powerful and active accelerator combination. In the course of this paper Hendricks points out that, with certain commonly used accelerators in GR-S, while there is in general a decrease in ultimate elongation with increase in time of cure, after aging in the air-oven there is actually in some cases an increase in elongation with time of cure. The heat stability is, therefore, better at overcures.

Work in this laboratory has led us to these same two general conclusions, which suggest the broader generalization that, to secure good heat stability and otherwise satisfactory vulcanizates, there must be low sulfur, powerful acceleration and a tight cure

EFFECT OF OVERCURING ON HEAT STABILITY

While agreeing in the main with Hendricks's conclusions, and being able to confirm many of the observations in his paper and in some of the other papers quoted, recent work carried out throws fresh light on the general problem of the effect of accelerators on heat stability, and, for this reason, is worth recording.

The fact that overcured GR-S vulcanizates show better heat stability than those which have received shorter cures has long been recognized in this laboratory, and the experiments quoted below were carried out to investigate the effect of very drastic overcures.

The following two stocks were mixed:

S. 358	A	B
GR-S	100	100
Micronex W-6	40	40
Zinc oxide	2.5	2.5
Stearic acid	2	2
Tackol (Grade 2)	4	4
Sulfur	2	2
Santocure	1	1
Mercaptobenzothiazole	...	1
Diphenylguanidine	...	0.25

Slabs were cured as follows, and tensile properties were determined from them by the A.S.T.M. technique.

- (1) A normal press-cure of one hour at 141° C.
- (2) A press-cure of 24 hours at 141° C.
- (3) A press-cure of 1 hour at 141° C, followed by 23 hours at 100° C.

Compound	Cure	Modulus at 300% elongation	Tensile strength	Elongation at break (percentage)
S. 358-A	(a)	1042	1930	456
	(b)	1272	2200	420
	(c)	1372	1880	380
S. 358-B	(a)	835	2190	565
	(b)	1325	1810	360
	(c)	1202	1900	420

(All stress figures in lbs. per sq. in.)

A duplicate series of cures was then aged for 24 hours at 100° C in the air oven, and tensile properties after aging were determined (+ $\Delta M\%$ means the percentage increase in the 300 per cent modulus due to aging, and - $\Delta E\%$ is the corresponding fall-off in elongation at break).

AGED RESULTS

Compound	Cure	Modulus at 300% elongation	Tensile strength	Elongation at break (percentage)	+ $\Delta M\%$	- $\Delta E\%$
S. 358-A	(a)	...	1510	250	...	45
	(b)	1368	2040	400	8	5
	(c)	1700	1940	340	24	11
S. 358-B	(a)	...	1765	340	...	40
	(b)	1387	1830	360	5	0
	(c)	1468	1780	350	22	17

There is in these results a comparison between air-oven aging for 24 hours at 100° C and overcuring in the press for 23 hours at 100° C. To afford a similar comparison between overcuring and oven aging for 23 hours at 141° C, further slabs were cured and aged as indicated, with the following results.

Compound	Cure at 141° C	Aged at 141° C	Modulus at 300% elongation	Tensile strength	Elongation at break (percentage)	- $\Delta E\%$
S. 358-A	60 min.	23 hrs.	...	760	100	78
S. 358-B	60 min.	23 hrs.	...	1130	150	73

This work leads to the following conclusions.

The effect of air-oven aging for a given time at a given temperature is far more severe than overcuring in the press for a similar time at a similar temperature. The relevant differences between the two processes are the absence of air during a press overcure, and possibly the fact that the overcuring process was continuous, while in the aging experiment the vulcanizate necessarily had a short respite between curing and aging.

The effect of these drastic overcures on the unaged tensile properties is comparatively slight in both cases, and there appears to be little difference between the effect of an overcure of 23 hours at 141° C and 23 hours at 100° C. The overcures cause modulus increases in both cases, but in the case of the Santocure-accelerated stock these are very small, although Santocure, a thiazole derivative, would normally be considered a persistent accelerator. The overcured stocks show much better heat stability than those which have received a normal cure, while in both compounds the cure of 24 hours at 141° C gives better aged results than the less drastic overcure.

Such overcures are of course quite impracticable, but it is felt that this work is interesting for the light it throws on the vulcanization process and on the heat embrittlement of GR-S vulcanizates.

EFFECT OF VARIOUS ACCELERATORS

A further series of experiments was carried out, using various accelerators, to determine in which cases this effect of improved heat stability after longer cures is observed. The stocks mixed were as follows.

S. 363	S	T	U	V	W	X
GR-S	100	100	100	100	100	100
Micronex W-6	40	40	40	40	40	40
Zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	1	1	1	1	1	1
Tackol (Grade 2)	4	4	4	4	4	4
Sulfur	2	2	2	1.35	1.5	2
Santocure	1	1	...
Mercaptobenzothiazole	...	1.5	1	0.7
Diphenylguanidine	0.25	0.9
A-32	0.5	...
Thiuram MSM	0.35

Slabs were cured from these stocks as shown, and two dumb-bells from each slab were tested unaged, while the other two were aged for 24 hours at 100° C in the air-oven before testing.

Results are given below:

Stock	Cure at 141° C (min.)	Unaged			Aged 24 hours at 100° C in air				
		Modulus at 300% elongation	Tensile strength	Elongation at break (percent-age)	Modulus at 300% elongation	Tensile strength	Elongation at break (percent-age)	$\Delta + M\%$	$-\Delta E\%$
S. 363-S	20	368	1170	710	...	1495	240	...	66
	40	875	2120	530	1950	1950	300	120	43
	60	1060	1980	460	...	1720	280	...	39
	80	1100	1920	440	...	1590	280	...	36
S. 363-T	20	93	315	870	430	1450	690	360	21
	40	309	1385	800	892	1675	465	190	42
	60	512	1640	640	1135	1500	390	120	39
	80	635	1945	635	1190	1735	405	88	36
S. 363-U	20	324	1245	765	1305	1485	340	300	56
	40	702	1935	580	1560	1710	330	120	43
	60	910	1845	490	1620	1790	330	78	33
	80	995	1980	490	1540	1540	300	55	39
S. 363-V	20	612	1750	640	1385	1500	320	110	50
	40	695	1830	565	1170	1790	440	68	22
	60	770	1885	565	1135	1750	430	60	24
	80	760	1680	530	1075	1750	445	41	16
S. 363-W	20	675	2480	660	1810	1810	300	170	55
	40	787	2280	575	1555	1850	340	98	41
	60	792	2170	545	1440	2060	390	82	28
	80	855	2600	590	1330	1990	415	56	30
S. 363-X	20	450	1840	750	927	1735	475	106	37
	40	630	2000	630	1110	1700	430	76	32
	60	657	1955	610	1090	1820	440	66	28
	80	660	2140	610	1145	2080	470	74	23

From the experiment it can be concluded that, with all the accelerator combinations used, heat stability improves with increasing time of cure. Embrittlement, measured by increase in modulus on aging, tends to a fairly stable level in all cases at the longer cures, but elongation fall-off figures show a definite if small advantage for the low sulfur stocks and for tetramethylthiuram monosulfide acceleration with normal sulfur. Stock S. 363-V with

very low sulfur and molecular proportions of mercaptobenzothiazole and diphenylguanidine shows the best heat stability. Good results from this formulation were claimed in a recent publication.

LOW SULFUR FORMULATIONS

Some further low-sulfur formulations were tested to confirm the conclusions of the last experiment. The following stocks were mixed.

S. 363	A	B	C	D	E
GR-S	100	100	100	100	100
Micronex W-6	40	40	40	40	40
Zinc oxide	2.5	2.5	2.5	2.5	2.5
Stearic acid	1	1	1	1	1
Tackol (Grade 2)	4	4	4	4	4
Sulfur	2	1.35	1.35	1.35	1.35
Mercaptobenzothiazole	1	0.7	1
Benzothiazyl disulfide	1	0.7
Diphenylguanidine	0.25	0.9	0.6	0.6	0.9

S. 363-A was a conventional type mix to act as a control. S. 363-B contained equimolecular proportions of mercaptobenzothiazole and diphenylguanidine and S. 363-D equimolecular proportions of benzothiazyl disulfide and diphenylguanidine. Slabs were cured as shown below, and were tested by A.S.T.M. technique before and after oven-aging at 100° C. The results are quoted at top of next page.

These results are even more striking than those of the previous experiment. They show clearly that high accelerator-low sulfur stocks have good non-persistent qualities, and possess much better heat-stability than the control; again this effect is more marked in the vulcanizates which have been given the longer cures. There appears to be some advantage for the stocks containing molecular proportions of mercaptobenzothiazole-diphenylguanidine and benzothiazyl disulfide-diphenylguanidine, respectively, although these proportions do not appear to be critical.

Some further stocks were mixed to show the effect of varying concentrations of sulfur in a GR-S tread-mix accelerated with a Santocure-A-32 combination. The formulations were:

S. 364	A	B	C	D	E
GR-S	100	100	100	100	100
Micronex W-6	40	40	40	40	40
Zinc oxide	2.5	2.5	2.5	2.5	2.5
Stearic acid	1	1	1	1	1
Tackol (Grade 2)	4	4	4	4	4
Sulfur	2	1.2	1.4	1.6	1.0
Santocure	1	1	1	1	1.2
A-32	...	0.5	0.5	0.5	0.5

Slabs were cured as shown at bottom of page 162, and were tested by the A.S.T.M. technique, before and after oven-aging at 100° C.

The effect of using low-sulfur formulations on heat-stability is again most marked, and it is clear that the lower the sulfur the better the heat stability, as judged by the percentage elongation fall-off due to aging. The vulcanizing combination of Santocure and A-32 gives consistently good tensile strength and elongation figures, and, as with the previous results quoted, the tensile strengths are maintained to a remarkable degree after aging.

Stock	Cure at 141° C (min.)	Unaged			Aged 24 hours at 100° C in air				
		Modulus at 300% elongation	Tensile strength	Elongation at break (percentage)	Modulus at 300% elongation	Tensile strength	Elongation at break (percentage)	+ΔM%	-ΔE%
S. 363-A	30	690	1980	605	1520	1690	340	120	44
	60	929	1870	490	...	1410	270	...	45
S. 363-B	30	736	2000	600	1152	1895	445	56	26
	60	756	1705	530	1050	2040	480	39	9
S. 363-C	30	692	1810	580	1242	1735	405	80	30
	60	745	1813	547	1105	1730	435	48	20
S. 363-D	30	701	1970	610	1162	1955	430	66	29
	60	745	1730	530	1062	2090	505	43	5
S. 363-E	30	656	1940	610	1052	2160	540	60	11
	60	666	2020	620	969	2020	515	46	17

In all these stocks it is apparent that a flat modulus-time of cure relationship and relatively good heat stability tend to go together. It is felt that the idea that this effect is due to the accelerator being nonpersistent is only a part truth, and that it would be more correct to say that the vulcanizing combination, accelerators and sulfur, was nonpersistent in these cases, since similar accelerator combinations with higher sulfur contents have been shown to give sharply rising modulus-time of cure curves and poor heat stability.

GENERAL CONCLUSION

With moderately powerful acceleration an excess of sulfur is necessary to give the requisite properties in a reasonable vulcanizing time. In such cases there is excess "embrittlement potential" left after curing, and after aging in air at an elevated temperature, embrittlement takes place, probably by some reaction or reactions involving cross-linkage formation. If such a moderately accelerated stock is overcured, the vulcanizate emerges at a lower embrittlement potential, and consequently shows better heat stability. But

Stock	Cure at 141° C (min.)	Unaged			Aged 24 hours at 100° C in air				
		Modulus at 300% elongation	Tensile strength	Elongation at break (percentage)	Modulus at 300% elongation	Tensile strength	Elongation at break (percentage)	+ΔM%	-ΔE%
S. 364-A	30	676	1920	580	...	1633	253	...	55
	60	930	1855	475	1760	1760	300	89	37
S. 364-B	30	644	2310	680	1162	2260	480	80	29
	60	630	2020	615	949	2250	545	50	11
S. 364-C	30	690	2270	635	1292	2135	445	87	30
	60	718	2313	623	1105	2380	530	54	15
S. 364-D	30	846	2310	570	1550	2020	350	83	39
	60	918	2150	525	1407	2180	420	53	20
S. 364-E	30	566	2010	665	1036	2410	555	83	17
	60	611	2160	665	856	2250	595	40	11

since such overcures do not give very desirable physical properties in the first place and are, furthermore, costly and impracticable, it would appear preferable to use low sulfur formulations with very powerful but nonscorching accelerators or accelerator combinations to achieve the same result.

In this work only one aspect of the problem has been considered, and the effect of using formulations of the type quoted on the heat build-up and tear resistance of the respective vulcanizates has not yet been assessed. It is fully

expected that compromise will be necessary to attain an all-round advantage. Further work is in hand in these laboratories and it is hoped to provide a more complete report at a later date.

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EFFECT OF MILLING ON PROPERTIES OF HEVEA AND BUNA RUBBERS *

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Most studies of the hysteresis and heat build-up properties of rubber polymers have been carried out at relatively low strains, corresponding to not more than 100 per cent. The data have shown that GR-S has more hysteresis than Hevea. Using repeated extensions to fixed loads, Rohde¹ in 1939 showed that for tensile stresses above 500 pounds per square inch (corresponding to about 150 per cent stretch on the first extension) Buna-S showed less hysteresis than natural rubber. By generating the hysteresis loops to fixed extension

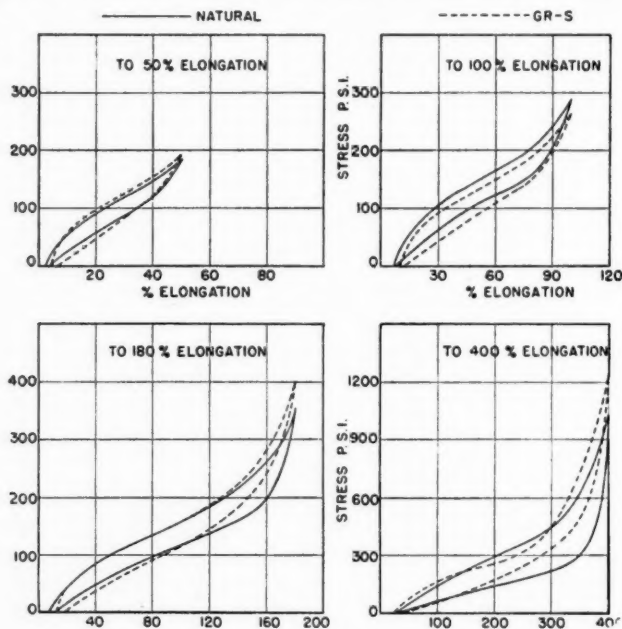


Fig. 1.—Hysteresis loops for natural rubber and GR-S treads (tenth loop).

rather than to fixed loads (Figure 1) it was recently shown² that not only was there a reversal in relative hysteresis rating (Figure 2) but that at the higher elongations both the extension and retraction curves of GR-S lie above those of the natural rubber. Thus at the higher elongations GR-S not only has less hysteresis but, after preworking, is stiffer than natural rubber.

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This fact appeared to be significant in the problem of cut-growth failures of GR-S tires. In a rolling tire the rubber is strained while making contact with the road, is held for a short time in this strained position, and is then released as it leaves the road. This occurs during about one-sixth of the revolution. During the remaining five-sixths of the revolution the rubber is allowed to recover. At the apex of a growing cut this strain reaches breaking elongation. As the apex of a growing cut nears an element of tread rubber in its path, that element is subjected to a series of stress-strain cycles or hysteresis loops of progressively greater severity.

A natural rubber and a GR-S tread compound were therefore subjected to a succession of extensions and retractions, and the effects on modulus,

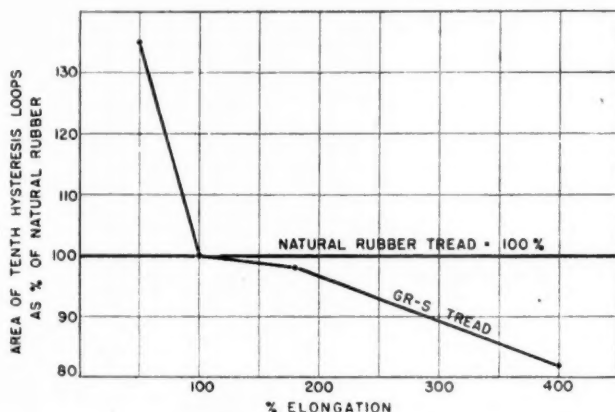


Fig. 2.—Effect of elongation on hysteresis of GR-S and natural rubber.

breaking elongation, and tensile strength were determined. Using a tensile testing machine operating at standard speed (jaw separation of about 20 inches per minute), dumbbell test-pieces were stretched ten times to 100% E , then ten times to 200%, up to ten times ($N \times 100\% E$). (The limiting value for N was determined empirically in each case.) They were then immediately broken, and the stress-strain curves generated in the conventional manner. The results are shown in Figure 3 where the values of $N \times 100\%$ are shown in the circles on the curves of the preworked samples. It is seen that natural rubber increases progressively in breaking elongation (from 700 to 900%). Its tensile strength, although declining, always remains higher than that of GR-S. On the other hand, GR-S gives no evidence of such relaxation or lengthening.

This relaxation failure in the case of GR-S has an important bearing on the forces which operate to extend a cut. The "preworked" modulus values correspond closely to equilibrium stresses. The following comparative figures are taken from Figure 3:

Maximum cyclic preworking	Modulus (lbs. per sq. in.)					
	300%		500%		600%	
	Hevea	GR-S	Hevea	GR-S	Hevea	GR-S
300%	450	500	1750	1600	2500	2025
500%	75	100	750	900	1600	1950

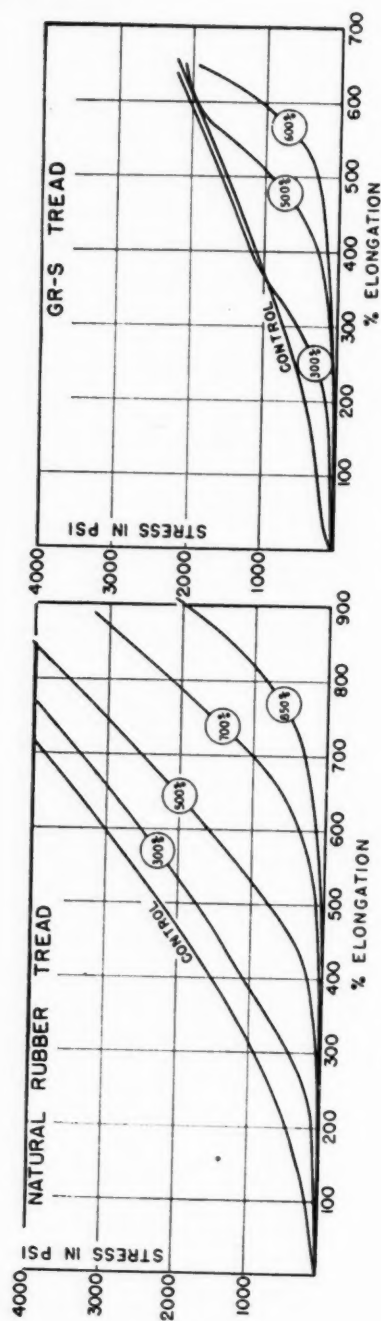


FIG. 3.—Effect of progressive flexing on stress-strain properties of natural-rubber and GR-S treads.

When the samples were preworked to low elongations (up to 300 per cent), the more plastic properties of GR-S showed up in the form of prevailing lower modulus values. But when the preworking was carried to high strains, such as those encountered in the path of an advancing or growing cut, Hevea relaxed and developed the lower retractive stresses. Despite its lower tensile strength, GR-S retained higher equilibrium modulus values.

The relaxation or lengthening of cured Hevea tread stocks, through repeated working at high extensions, may be regarded as analogous to oxidative scission or breakdown. This phenomenon is difficult if not impossible of attainment in the case of vulcanized GR-S, where the prevailing tendency is a shortening or hardening, due to gel or cross-linked structure development. It was therefore decided to approach the problem from a different angle. A study of milling conditions was decided on in the hope that suitable conditions of mastication, with carefully controlled temperatures, might result in a softening or lengthening of the GR-S tread stock due to one or more of the following factors:

1. Breakdown of the cross-linked or gel structure itself.
2. Deflocculation of the carbon black, resulting in lowered modulus, increased breaking elongation, together with increased tensile strength.
3. More perfect disposition or lodgment of the carbon particles as a continuous-phase enveloping and bonding the discrete polymer units, resulting in improved reinforcement coupled with higher subpermanent set.

The effect of milling technique and procedure was the first factor investigated. At conventional temperatures (130° F, water circulating continuously), the initial series of comparative studies between Hevea and some synthetics are summarized.

REMILLING AT NORMAL TEMPERATURES

The quality of a rubber compound depends not only on the kind and particle size of the reinforcing pigment selected but also on the degree of dispersion

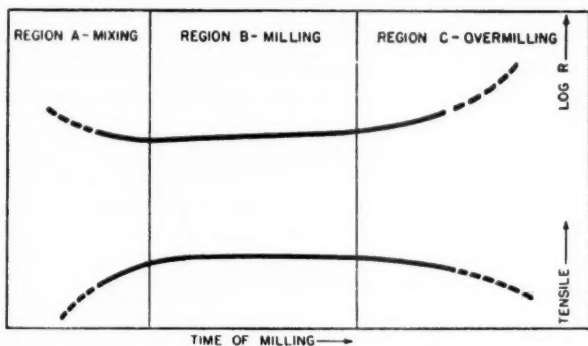


FIG. 4.—Progress of log R and tensile with time of milling (schematic).

of the pigment. The importance of proper milling and of correct order of mixing has been emphasized for many years.

Carbon blacks in general, and the finer or channel carbons in particular, require careful attention in the mill room to secure maximum reinforcement.

Optimum dispersion is not easily obtained and is difficult to evaluate. The degree of dispersion is frequently judged by the gloss and texture of cut or torn surfaces, directly or with the microscope. These methods are far from satisfactory, since for carbon black, "true dispersion of carbon black (in rubber) begins where the microscope leaves off".

TENSILE STRENGTH AND ELECTRICAL RESISTIVITY.—As a control over the proper amount of milling or processing of natural-rubber tire treads, it has been found in these laboratories that the electrical resistivity of either the raw or cured stock is a quick and useful test. As illustrated in Figure 4, the tensile strength of a tread stock passes through a maximum and the electrical resistivity through a minimum as time of milling is increased. Three stages may be recognized:

Region A.—In the early or mixing stage, free or unreinforced rubber disappears and tensile increases. Large aggregates of carbon simultaneously disappear, conducting flocculates or chains of carbon multiply, and electrical resistivity ($\log R$) eventually reaches a minimum.

Region B.—The second stage of milling can be described as the bonding stage, where the carbon is further distributed or lodged within the rubber phase. There is some disaggregation of the rubber, which increases its surface and so increases $\log R$ slightly. On balance, reinforcement of the rubber, through more complete lodgment of the carbon, dominates over breakdown of the rubber itself and tensile continues to rise.

Region C.—In the overmilling stage, disaggregation of the rubber takes over, tensile falls off, and, through the development of considerable new rubber surface, electrical resistivity rises sharply.

Direct-current resistivity thus affords a clue to optimum processing of a natural rubber tread compound. It has repeatedly been found useful as a control for the factory processing of such compounds.

EFFECT OF REPEATED REMILLING.—Figure 5 compares natural rubber with Perbunan (imported), Buna-S (GR-S), and Butyl-B when similarly processed on a 6 × 12 inch laboratory mill. In this case the first milling of the compounds produced normal laboratory mixes, the time varying for the various polymers and being particularly prolonged for Perbunan. This initial mixing was followed by alternate 24-hour test periods and 5-minute remillings, with water at 130° F circulating through the rolls; *i.e.*, no special effort was made to keep down roll or stock temperatures.

Natural Rubber.—Up to one remilling, tensile strength is in general maintained, without sensible loss in modulus or hardness and with little or no rise in elongation. It seems best milled when $\log R$ has reached a minimum.

Perbunan.—Best tensiles are reached only after two to four remillings. This has also noticeably increased elongation. Modulus and hardness have sensibly declined. At the end of the first remilling, $\log R$ is already rising rapidly, and so provides no clue to optimum dispersion. Milling time is dictated by practical considerations. If high tensile and elongation are desired, regardless of cost, extensive milling and remilling are indicated. Where modulus is to be maintained at its maximum, even at the sacrifice of some tensile, shorter milling time is indicated.

Buna-S.—The picture is similar to natural rubber only with respect to tensile strength; *i.e.*, tensile reaches its maximum at about one remilling. Modulus and elongation show similar and distinctive trends in that they also

have maxima at about one remilling. This falling off in elongation as Buna-S is overmilled is of prime importance because of the shortness and tenderness of Buna-S stocks under dynamic conditions. As with Perbunan, $\log R$ rises continuously and so affords no clue to optimum physical properties as processing proceeds. The possibility of $\log R$ minima for Buna-S and Perbunan is, however, not entirely precluded, since in this work undermillings were not carried to the extremes necessary to establish this point.

Butyl.—The picture appears to be more similar to that of Buna-S than to either of the other two polymers. Tensile and modulus reach a simultaneous maximum as in Buna-S. This indicates that in Butyl, as in Buna-S, maximum tensile can be, and probably should be, developed, since it involves no penalty in modulus. However, with Butyl this maximum occurred between two and three remillings, compared with one for Buna-S. The shortening of Butyl

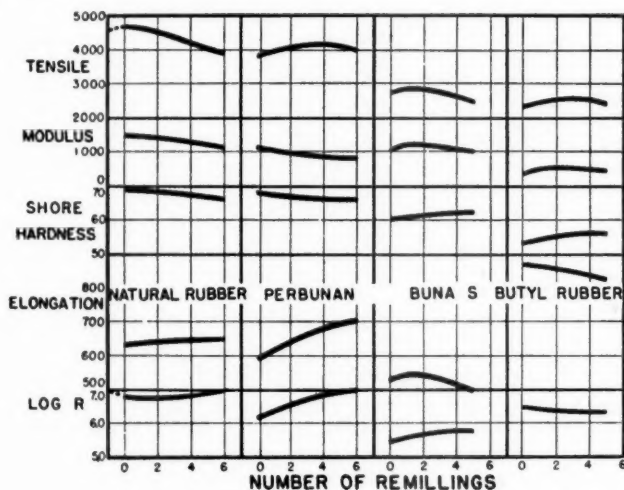


FIG. 5.—Effect of remilling on tread stocks.

elongation with remilling is less than that of Buna-S, and what loss occurs may be ignored against its background of excess. $\log R$, on the other hand, shows a slow but steady downward trend which may correspond to the left, or declining, arm of "natural rubber-carbon black" trends. This is rendered plausible by the softness of Butyl stocks, which would be expected to lengthen this declining left arm of the resistivity *vs.* milling trend.

COMPARISON OF HOT AND COLD MILLINGS

Of particular interest in the preceding comparative study was the distinctive and serious decrease in elongation of GR-S on repeated milling. Because of the large surface area of reinforcing carbon blacks, a need appeared for severe milling to assure adequate dispersion or carbon surface development in the GR-S, particularly since it is handicapped with low gum strength.

The temperature build-up resulting from ordinary high-viscosity milling techniques is undesirable for GR-S because of its shortening tendency. Gordon plastication or other hot milling of raw GR-S effects an apparent improvement in the dispersion of the carbon black introduced after hot plastication,

but this improvement is at the expense of increased modulus, decreased elongation, and impaired cut-growth resistance. A study of various combinations of temperature and milling conditions was indicated.

Raw GR-S was hot-plasticized by 30-minute milling in a laboratory Banbury, with the rotors and case heated to 270° F. Other lots of the same polymer were cold-refined by passing through a tight 6 × 12 inch mill with rolls at 80° F; the sheeted rubber was then festooned to facilitate cooling until the entire batch passed through the rolls. This was repeated twenty times. The results are summarized in Table I.

TABLE I
EFFECT OF HOT AND COLD PROCESSING ON GR-S

Treatment	Physical properties as percentage of normal laboratory-milled control				
	Modulus at 300%	Tensile at break	Elongation at break	Flex cut resistance	Hot-iron life
Raw GR-S hot-plasticized, 30 min., 270° F	161	82	69	12	7
Raw GR-S cold-refined, 20 passes, 80° F mill	96	105	107	247	350
Raw GR-S cold-refined, then hot-plasticized	134	82	73	23	5
Raw GR-S hot-plasticized, then cold-refined	127	78	75	47	4
Complete tread compound, cold-refined	85	106	111	310	111

Conclusions to be drawn from Table I are: (1) Hot plasticizing of GR-S shortens the rubber and detracts from heat and flex resistance. (2) Cold refining of GR-S lengthens the rubber and improves heat and flex resistance. (3) Cold refining does not protect GR-S from subsequent hot processing. (4) GR-S shortened by hot plasticizing is not restored by subsequent cold refining. (5) The benefits of cold refining apply also to the completely formulated tread compound.

These results invited an intensive investigation of the cold-refining approach. A preliminary series involving 20, 30, and 40 passes through the cold mill had not developed an optimum; the improvement in flex resistance and hot-iron life continued. Obviously GR-S, unlike natural rubber, was being fundamentally changed for the better in chemical or colloidal structure by the strenuous cold mastication. Disaggregation was being confined to the injurious gel and not extended to the long primary chains, since tensile strength as well as breaking elongation had improved. Either for better vulcanization, better reinforcement, or both, the structural deformities of the copolymer had apparently been lessened.

EXTREME COLD REFINING

The raw polymer and the complete tread compound were refined on cold laboratory rolls for a succession of passes up to 320. The results are shown in Figure 6. The curves illustrate the progressive lengthening effect of repeated cold refining, whether of GR-S or of the complete tread compound. Best all-round quality developed at the equivalent of about 50 passes of refining on the laboratory mill. Mill roll temperature was kept at 80° F, corresponding to a stock temperature of about 120° F.

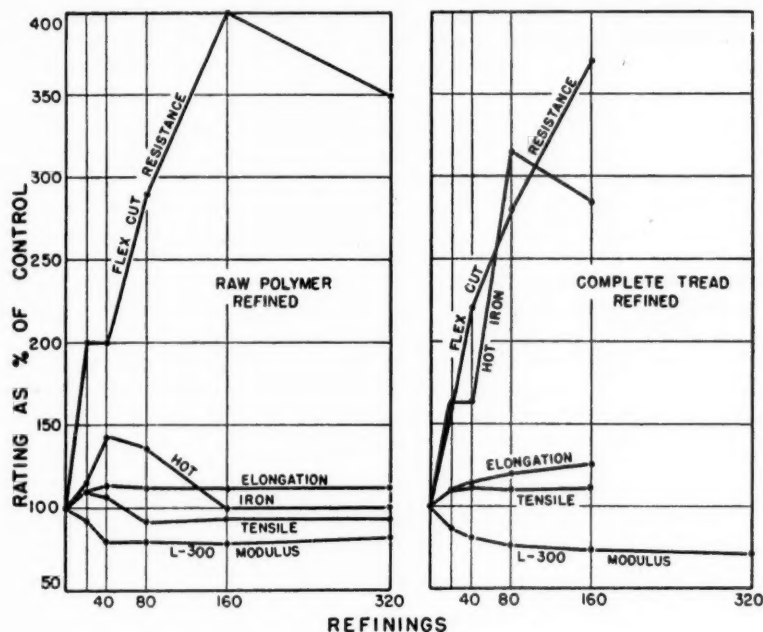


Fig. 6.—Effect of cold-refining of raw GR-S and of a GR-S tread compound on cut growth and thermal shortening.

SUMMARY AND CONCLUSIONS

1. The superior cut-growth resistance of Hevea tread stock is partly ascribed to its pronounced relaxation or lengthening when subjected to repeated severe cyclic extensions. Under such conditions the breaking elongation increases from 700 to 900%. GR-S under similar treatment fails to develop any lengthening.

2. As a consequence of this failure to lengthen under repeated severe strains, such as those antecedent to cut-growth failure, GR-S exhibits higher modulus, *i.e.*, at 500 or 600 per cent elongation, or higher retractive forces than does Hevea. This also promotes cut growth.

3. In Hevea, progressive milling (at normal temperature) of tread stocks tends to develop a tensile maximum. At this point of optimum milling, *d.c.* resistivity reaches a minimum. Overmilling, characterized by a decrease in tensile, shows a sharp rise in *log R*.

4. With Perbunan, highest tensiles and elongations are realized only after several remillings, at which point modulus and Shore hardness have already shown marked decline.

5. With Buna-S (GR-S), tensile and elongation reach their maxima at about one remilling (at normal temperatures). Milling beyond this point is reflected in sharp degradation of elongation. *Log R* provides no indication of optimum conditions, since it is rising at this point.

6. In Butyl B, tensile and modulus reach a simultaneous maximum between two and three remillings. *Log R* in this region is declining and reflects retardation due to the softness of Butyl stocks.

7. Hot milling of GR-S shortens and reduces heat and flex properties. Cold refining lengthens GR-S and improves these properties, but does not protect against subsequent damage from heat. GR-S shortened by heat cannot be restored by subsequent cold refining. The benefits of cold refining apply also to the completely formulated tread.

8. Extreme development of the cold-refining technique produces the following results (based on treatment of complete tread mixing): Modulus declines continuously to less than 50 per cent of control. Elongation increases continuously to 125 per cent of control. Tensile strength increases to 110 per cent at 20 passes and then remains steady. Hot-iron life (thermal shortening) improves continuously to 310 per cent at 80 passes. Cut-growth resistance improves progressively to 370 per cent of control at 160 passes, and is still rising.

9. The fact that such striking all-round quality takes place at about fifty cold refinings with rolls at 80° F (stock at about 120° F) suggests the importance, in the fabrication of GR-S tires and other products subject to dynamic usage, of (a) avoidance of elevated temperatures at all stages, and (b) further study of the remedial effects of strenuous mastication of refining of GR-S tread type, carbon-reinforced stocks under low-temperature conditions.

10. Attempts to improve GR-S should be oriented in two opposite senses: to decrease its hysteresis at low extensions (under 100 per cent) but to increase its hysteresis, or capacity to relax, at the higher extensions antecedent to cut growth.

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MORPHOLOGY OF LATEX PARTICLES AS SHOWN BY ELECTRON MICROGRAPHS *

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In the course of other work on the formation of latex in plants, it seemed desirable to examine the morphology of the particles under higher magnification than had been possible previously. Extensive microscopic work was carried out by Hauser¹ on latices from many plants. He also made use of a micromanipulator in a number of experiments that are widely quoted. Lucas² used the ultraviolet-light microscope for observations on particles in preserved *Hevea* latex. Recent availability of the electron microscope makes possible an extension of observations on latices.

Micrographs were made with an R.C.A. Type B electron microscope. The construction and operation of this microscope have been described elsewhere³. In this instrument the specimen is placed in a high vacuum; the pressure is about 10^{-4} millimeters of mercury. The micrographs were made in most cases at an initial magnification of 4,000–8,000 diameters and were further enlarged optically. Particular advantages of the electron microscope compared with usual and ultraviolet microscopes are its greater depth of focus and resolving power. The number of particles examined on a film, however, is restricted by the high magnification and the great dilution of the sample necessary to obtain separate particles. A large number of particles were observed before micrographs were taken, and it is considered that those reproduced here are typical.

Latex samples were generally diluted with 1 per cent ammonia until only faintly turbid. A drop of the dilute suspension was dried at room temperature on a thin Formvar film supported on a 200-mesh nickel screen, which was cut to be placed on a holder for inserting into the microscope. *Hevea brasiliensis* (H.B.K.) Muell. Arg., *Hevea spruceana* (Benth.) Muell. Arg., *Taraxacum kok-saghyz* Rodin, *Cryptostegia grandiflora* R. Br., *Asclepias syriaca* L., *Ficus elastica* Roxb., and *Castilla elastica* Cerv. latices were obtained locally. Plants approximately one year old of the first five species were brought to the microscope room to serve as an immediate source of latex supply. Several samples of *Taraxacum kok-saghyz*, *Ficus elastica*, and *Hevea brasiliensis* latex were diluted with distilled water only before drying on the Formvar film. Latex generally was obtained from the base of a petiole severed midway along the plant. In the case of *Taraxacum kok-saghyz* it was obtained from the lowest portion of the root.

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Manihot glaziovii Muell. Arg., *Funtumia elastica* (Preuss) Stapf, *Vallisneria spiralis* (L.) K. Schum., *Mascarenhasia elastica* Schum., *Alstonia scholaris* (L.) R. Br., *Mimosa pudica* (L.) Gaertn., *Landolphia droogmansiana* Wildem., and additional *Hevea brasiliensis* latices, preserved in 2 per cent ammonia and taken from plants five to fifteen years old, were obtained from the U. S. Plant Introduction Garden at Cocoanut Grove, Fla., through the courtesy of J. H. Heuer and J. A. Elder. *Manihot dichotoma* latex from the same location was preserved in 2 per cent sodium carbonate. Since these latices were not examined until a week after collection and were necessarily shipped, they might have undergone some change. The main purposes in examining them were to seek for unusually shaped particles that might have withstood this treatment and to get some information on latices from relatively old plants.

EXPERIMENTAL RESULTS

The limitations and restrictions of the electron microscope must be borne in mind in this discussion of results. To study a latex specimen it must be diluted, dried on to a Formvar membrane, and then placed in the vacuum of the microscope and photographed. The liquid particles wet the membrane to some degree and spread. In some cases this spreading brings two or more particles into contact, and they may then flow together. Volatile components which may be present are evaporated, with a possible further change in shape. Any nonvolatile substances either suspended or in solution in the water with the latex particles will still be present in the specimen and contribute to the background in various ways.

Results obtained are illustrated by the accompanying electron micrographs, the most striking features of which are pointed out in the legends. Particles which were spheres in the original latex are always flattened to various degrees. Some idea of the amount of flattening can be obtained by a comparison of the optical density at the center and edges of the particle in the micrographs. The extremes of flattening are illustrated by the micrographs of *Cryptostegia* (Figure 3D) and *kok-saghyz* (Figure 3C). A break in the mounting membrane of a *kok-saghyz* specimen gave an opportunity for making observations approximately parallel to the film surface (Figure 4). This shows the particles in profile to be lens-shaped, and to have diameters about three times the heights.

Morphological features of *Hevea brasiliensis* latex particles are in general similar to those described in detail by Lucas². The smallest particles are about 0.03-micron in diameter. So-called pear-shaped particles, long considered to be characteristic of *Hevea* latex, are apparent in Figure 1. They also were observed on electron micrographs of other latices. These pear-shaped particles appear to be formed by coalescence of small spheres. Latex particles in *kok-saghyz* are smaller than found for *Hevea*; the smallest observed particle is of the order of 0.01-micron in diameter (Figure 3C).

None of the other latices examined contained particles less than 0.1-micron in diameter, and all showed evidence of coalescence similar to that illustrated in the figures. It is, of course, possible that the smaller particles may have been destroyed in the latex samples shipped from Florida. Particles in the latex from *Mimosa* and *Castilla* were several microns in diameter, and showed a pronounced tendency to flatten, indicative of considerable fluidity. *Ficus*, *Funtumia*, and *Mascarenhasia* latex particles were similar in morphology to those illustrated for *Hevea*.

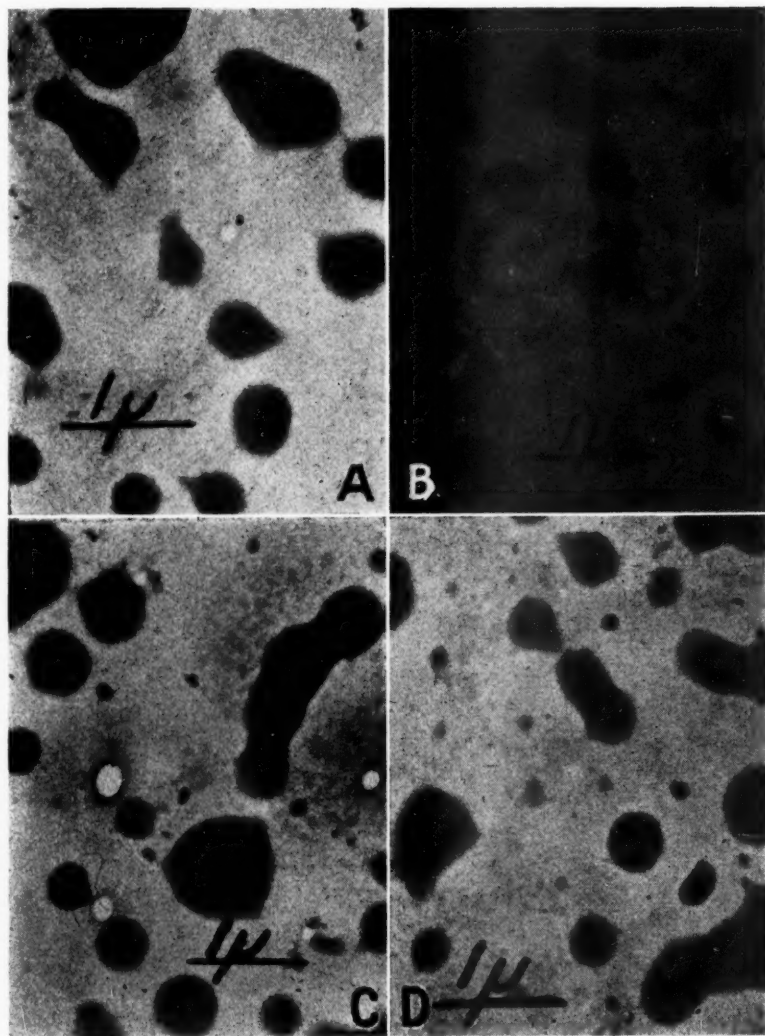


FIG. 1.—Electron micrographs of *Hevea brasiliensis* latex particles.

A. Large particles approximately 0.6 micron in diameter. Several pear-shaped particles show evidence of coalescence of small spheres. B. A chain more than two microns in length in which spherical particles are incompletely coalesced is prominent in the upper part of the micrograph. Small particles less than 0.1 micron in diameter can be observed below this chain. Some of these smaller particles are incompletely coalesced into groups of two or more particles several tenths of a micron in length. C: Particles ranging from about 0.03 micron to 1.0 micron in diameter. A chain formed by coalescence of at least four particles with diameters near 0.5 micron is present. Transparent circles in this and other micrographs are holes in the Formvar supporting film. D. Surface irregularities (indicated by arrows) on large particles indicating coalescence of small spheres (circa 0.03 micron in diameter). Mottling in the background of this and other micrographs is in part due to action of ammonia, used to prevent coagulation, on the Formvar film.

Electron micrographs (Figure 2) of *Manihot glaziovii* latex from a fifteen-year-old tree show the characteristic rod-shaped particles previously observed with light microscopes¹. Spherical particles, as observed by Memmler⁴, which

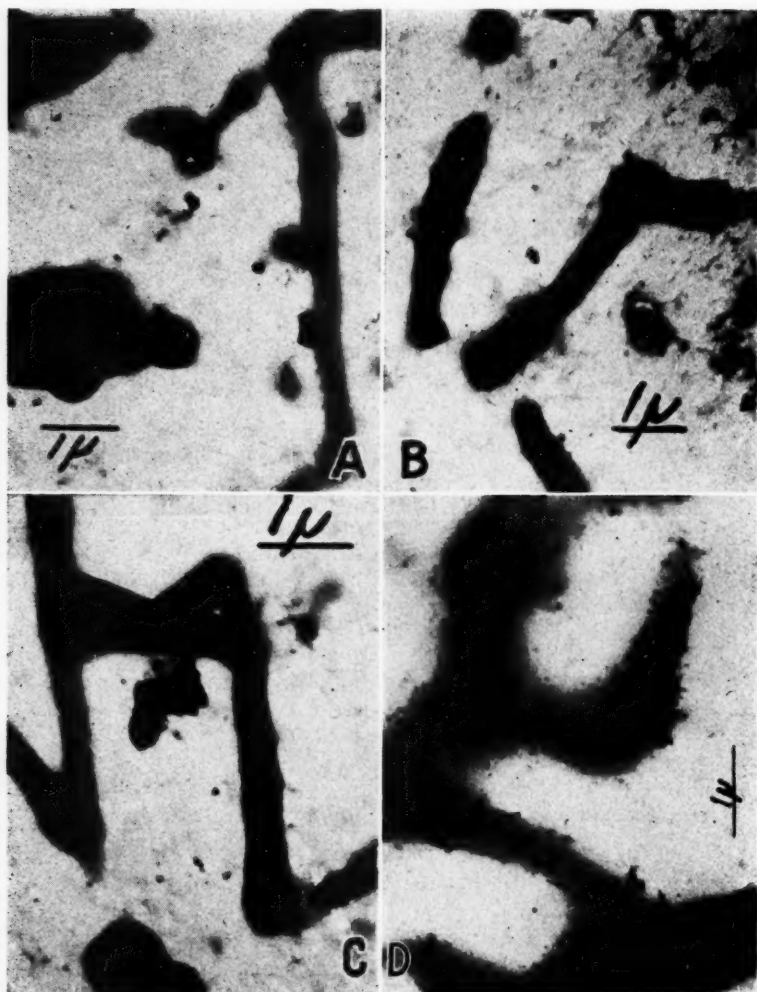


FIG. 2.—Electron micrographs of *Manihot glaziovii* latex particles.

A, B, and C. Rod-shaped particles several microns in length and about 0.5 micron in diameter. Round particle having approximately the same diameter as the rods is indicated by arrow in B. These particles can also be seen as parts of some of the rods. The contrast at the particle boundary is greater for *Manihot* latex than for *Hevea*. A filamentous material that can perhaps best be described as fuzzy is present at the particle boundaries. D. Creamed *Manihot* latex. The boundary surfaces of the rods are disrupted, and coalescence is apparent.

are said to be predominant in latex of young trees, are also revealed by the electron micrographs. The diameters of both flattened rods and spheres are approximately the same, and the rods give evidence of containing incompletely destroyed spheres. Freundlich and Hauser², from experiments with a micro-manipulator, concluded that the rods consisted of tough, homogeneous material.

While the boundaries of the rods of *Manihot glaziovii* are quite sharp in some cases, in others the boundaries have become vague and the rods quite

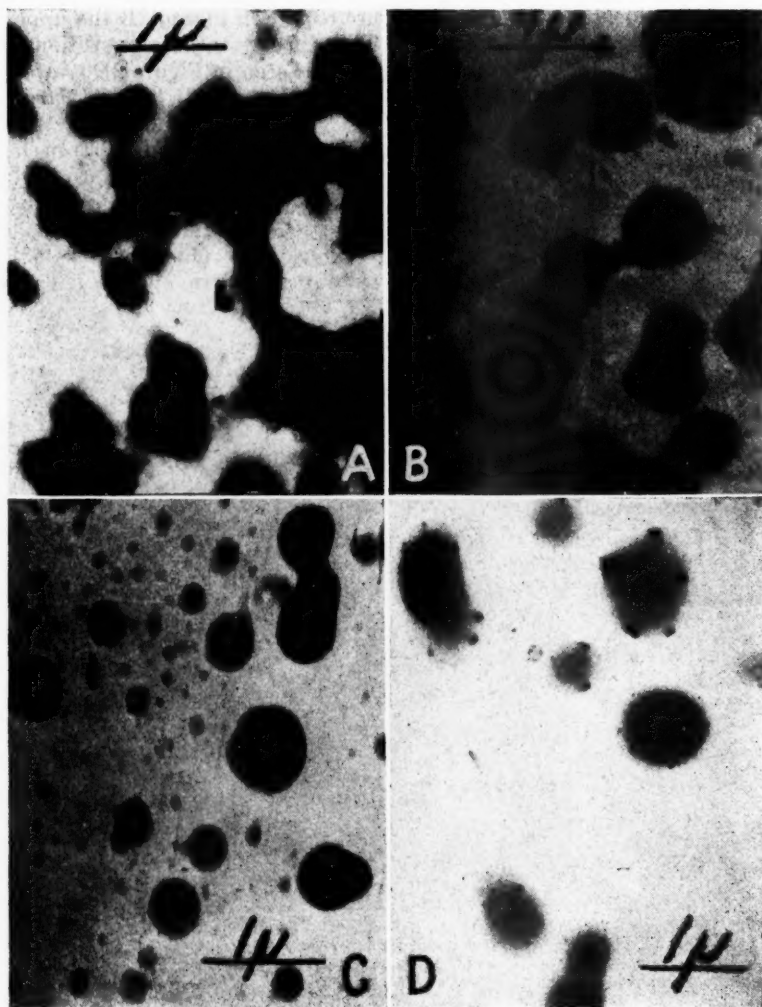


Fig. 3.—Electron micrographs of various latex particles.

A. *Funtumia elastica*. A partially coalesced mass showing some particles about 0.4 micron in diameter. In the upper half of the photograph, ten or more of these particles are joined in an irregular chain. Boundaries of the mass are thin and irregular. B. *Hevea spruceana*. Particles about 0.3 to 0.6 micron in diameter are coalesced into chains whose boundaries are regular though thin. C. *Taraxacum kok-saghyz*. Very small particles with distinct boundaries. The contrast on even very small particles is pronounced, indicating that the particles are not so greatly flattened on the supporting film as they probably are in B and D, and Figure 1 A-D. D. *Cryptostegia grandiflora*. Very fluid particles showing low contrast. The more opaque small fragments around the edge of the particles may be another latex component.

flattened. An example of such a case is shown in Figure 2D. Much finely divided granular material is seen along what appear to be the former rod boundaries. While the source and nature of this granular material are not known, its relative opacity indicates that it is of a much higher atomic density than the rubber. Granular material was also observed to a lesser extent in several other latices, as is illustrated by the micrographs of *Cryptostegia*

(Figure 3D) and *Manihot glaziovii* (Figure 5D). In Figure 2B the upper rod shows a vague outline in the center. This appears to be a transitional step between the sharp rods and material such as is seen in Figure 2D. A similar phenomenon was also noted for several rounded particles in balata (*Mimusops*) latex.

Less well-developed rod-shaped particles are shown on electron micrographs (Figures 5A and D) of a second sample of *Manihot glaziovii* latex. A picture of *Manihot dichotoma* latex that had been preserved with sodium carbonate is shown in Figure 5C. These particles instead of being rod-shaped are round. Some rod-shaped particles, obviously not rubber, are also present. It is possible that they are produced by the preservative, and are not charac-



FIG. 4.—Electron micrograph of *Tarazacum kok-saghyz*.

Torn portion of Formvar supporting film showing latex particles in profile. The particles are partially deformed by the folds of the film.

teristic of the latex. Observations under an oil immersion lens indicated the presence of rod-shaped particles having no observable birefringence.

DISCUSSION OF RESULTS

It was of interest to find such extremely small particles in some cases. The smallest particles must be composed of only a few molecules, since their size is of the order of 0.01-micron (10^{-6} centimeter), and they are flattened and probably contain some material other than rubber. Thus the molecular weight in such a particle, if it contained but a single molecule, would be considerably less than 300,000. This is well within the molecular weight range of rubber (50,000–1,000,000).

Observations of this and earlier work indicate that latex particles in many plants have form-retaining as well as fluid properties. The fluid property is

clearly necessary for coagulation of a latex; while form retention is required for the existence of concentrated latices. Fluid properties on a microscopic scale were demonstrated by Freundlich and Hauser's experiments with probes on large latex particles. They are also evident in the electron microscope in

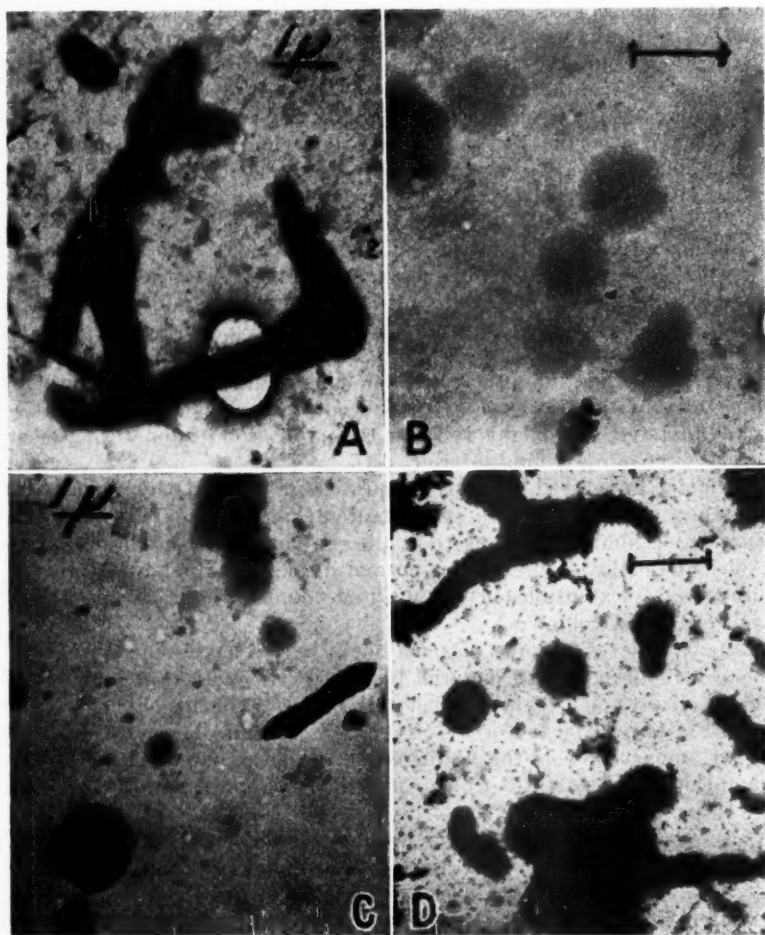


FIG. 5.—Electron micrographs of various latices.

A. *Manihot glaziovii*. Showing rodlike particles. B. *Ficus elastica*. A chain of three latex particles which have apparently united by restricted coalescence of the particles around points of contact. C. *Manihot dichotoma*. Round particles and an elongated nonrubber rod. D. *Manihot glaziovii*. Several spherical particles appear near the center of the micrograph and an irregular mass of partially coalesced spheres is shown near the bottom. An irregular rod-shaped particle is present in the upper left corner.

the flattening of particles and the binding together into masses. The form-retaining property is shown by persistence of particles containing partially assimilated spheres such as pear-shaped ones.

An apparently simple and direct explanation from these properties is that proposed by Freundlich and Hauser⁵, who postulated that the latex particles

are covered by a surface shell or film, with a more fluid interior. Kemp⁶ suggested that the film consists of an outer transitory liquid layer, an intermediate protein film, and an inner skin of gel rubber. The fluid interior is postulated to be an emulsion of sol rubber.

While this concept is simple, there is a serious argument against it: namely, a mechanism for separation of two fractions of rubber in the latex is implied. Gel and sol rubber have the same composition, as far as is known. They differ chiefly in their solubility in organic solvents. Gel rubber, by definition, is that portion of a rubber sample that swells rather than dissolves in solvents such as ether. It is reasonably held that this behavior is the result of "cross-linking" between portions of the hydrocarbon chain or chains in gel rubber. Since solubility depends to a great extent on similarity of solvent and solute, complete miscibility is expected for substances such as sol and gel rubber, which form the greater part of *Hevea* latex particles.

Properties of latex particles are equally in harmony with a simpler picture which should be general for long-chain polymeric substances. According to it, the molecules are simply intertwined as if they were odd lengths of string packed into a loose ball. If two such particles touch, loose ends and kinks of the molecules at the surface intertwine. One sphere, however, would be absorbed only slowly into another, and the shapes and retention of form would be expected. Withdrawing of an introduced probe would be expected to drag out some material, and might well give the impression of puncturing a surface film or layer covering a fluid interior.

The latter hypothesis perhaps explains more readily why some particles, such as those of *Cryptostegia* latex in Figure 3D, can be so greatly flattened on the supporting film. According to it, the contents of the whole particle could be sufficiently fluid to spread as a normal drop. The first hypothesis would require a readily extensible surface film to account for large changes in surface without change in volume.

Latex particles of *Manihot glaziovii* might indeed have some type of surface film of which the granular material in Figure 2D could be remanent. This would be an inversion of Freundlich and Hauser's conclusions⁵ that *Manihot* particles are tough and uniform. Several observations bear on this question; principal among these is the finding that the latex of young trees contains dominant spherical particles which ostensibly disappear by formation of rods as the trees age.

This formation of rods by union of spheres is also borne out by the electron micrographs, which give evidence of spheres combining in masses as well as in rods. Rod-shaped particles on close examination are found to be only approximately linear, and joined rods apparently form any angle. It would seem that, while spheres are forced into roughly linear aggregates, linear groups of spheres do not join collinearly.

There seems to be no reason why strictly physical factors, such as surface tension, Brownian motion, etc., irrespective of whether or not their operation is understood, should alone account for linear union of spheres in one latex and not in another. Two ways out of this impasse appear: namely, (1) some material favoring linear aggregation is present in *Manihot glaziovii* latex, or (2) a biological factor such as rod formation only at a particular site is operative. In the former case, by way of illustration, the material could be rubber itself, cellulose micelles, or starch molecules. In the latter case capture of spheres by a growing particle might take place only on contact with a cell wall.

The apparently slow increase of linear particles with age of tree might be in favor of some explanation of the latter type.

SUMMARY

Morphological features of particles from latices of sixteen plant species were studied by means of electron micrographs, a number of which are reproduced. The smallest particles have about the volume required to contain a very small number of molecules. Evidence is given for both form-retaining and fluid properties of latex particles. Difficulties with the hypothesis that these particles have fluid interiors covered by a surface film of gel rubber are pointed out. A new hypothesis accounting for the observed properties is advanced. According to it, the latex particles contain rubber molecules entwined as if they were odd lengths of string with other latex components held between the meshes.

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LOW-TEMPERATURE FLEXIBILITY OF SYNTHETIC ELASTOMERS

EFFECT OF AVIATION GASOLINES *

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Extreme low-temperature service conditions and new aviation fuels have the rubber industry confronted with the problem of designing stocks with low-temperature flexibility and solvent resistance. The accepted technique in providing such compounds has been that of selecting a suitable synthetic coupled with heavy plasticization. Such compounds, however, are inevitably leached free of plasticizer when immersed in fuels; the result is stocks having no greater freeze resistance than the same stock without plasticizer.

In many instances a lack of proper application analysis has caused stocks designed for low temperatures to fail in service, principally because field conditions of fuel immersion were neglected in the laboratory evaluation of freeze resistance. This inadequate analysis may be due in part to a lack of suitable instrumentation. Tests devised to measure bending characteristics, brittle points, and shatter points have lacked the delicacy and accuracy necessary in evaluating small but significant changes in thin sheet materials such as are used in hydraulic assemblies and in aviation carburetor diaphragms. The dynetensometer method has been employed in an analysis of freeze-resistant stocks under various simulated service conditions.

APPARATUS AND MATERIALS

The details of the tensiometer method were recently discussed by the present authors (cf. *The Rubber Age* (N. Y.) 53, 319 (1943)).

A Cenco du Noüy precision tensiometer, normally used for measuring surface tension, is modified and used in measuring modulus changes of rubber stocks. By determining the force required to bend a thin sample, acting as a cantilever beam, through a calculated deflection, relative stiffness at any temperature can be obtained.

In Figure 1 the large outer jar contains the cooling medium, tributyl phosphate, selected because of low solidification point and lack of fumes which might influence the flexibility of the samples. Temperature reduction is accomplished by addition of dry-ice. The carbon dioxide from the subliming dry-ice is supplemented by a stream of carbon dioxide gas from an external cylinder to exclude all moisture from the apparatus. Samples, moulded to a standard dimension of 1 inch long, $\frac{1}{4}$ inch wide, and $\frac{1}{50}$ inch thick, are fixed in clamps and located in the inner beaker where conditions of liquid immersion or air immersion may be secured. The clamping device (Figure 1) consists of an immovable clamp, into which $\frac{1}{2}$ inch of the sample is inserted, and a

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movable clip which is adjusted so that $\frac{1}{4}$ inch of the sample is exposed to the bending moment produced by the tensiometer. Two index marks are placed on the mirror behind the tensiometer arm and so spaced that a standard displacement or bending of the sample is secured when the instrument is operated.

The wire leading from the movable clip is attached to the tensiometer arm, which is then adjusted to the zero reading corresponding to the lower index mark. The knob at the right is turned until the arm moves to the upper index

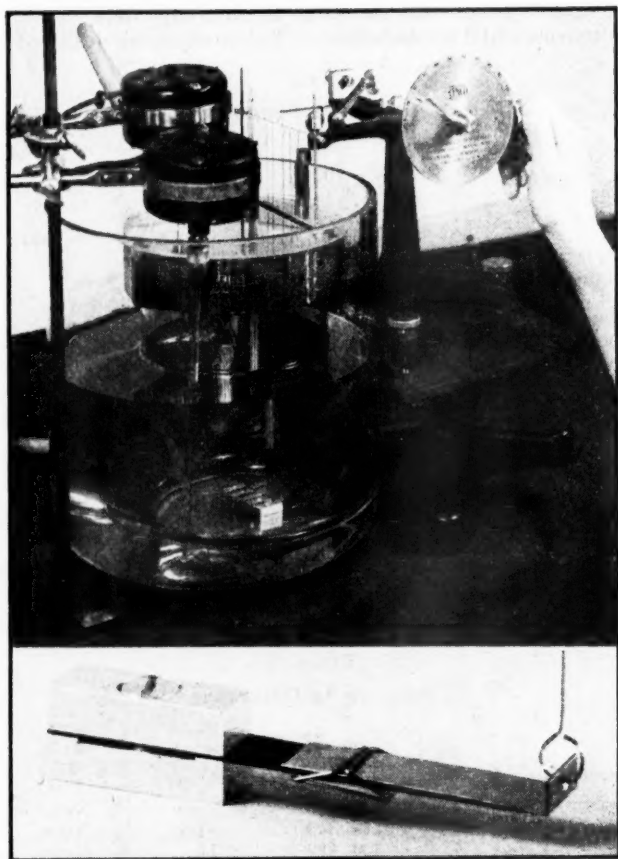


FIG. 1.—Modified precision tensiometer for measuring modulus change; close-up of clamping device (below).

mark. The scale reading thus obtained can be used in plotting a curve of stiffness against temperature.

The stiffening point is designated as that point at which a large increase in modulus occurs. It is the point where the force required to bend the sample raises the entire clamping apparatus, and is indicated on the graph by a dotted line extending to a point which would be approximately 2800 dynes (beyond the range of the instrument).

Elastomers.—The compounds investigated in this report were made up from

Hycar OR-15 and OR-25, Perbunan 26, and Neoprene FR and GN. Examination of numerous compounds of these base synthetics designed for low-temperature application has indicated that the basic freeze resistance of the compound is largely independent of formulation and compounding technique. Therefore, typical formulations were selected which appear to demonstrate general qualities of the various synthetics, and represent classes of compounds.

Plasticizer and carbon black proportions were kept the same throughout so that results should not be obscured by irrelevant factors due to compounding ingredients. Acceleration was the same in all compounds wherever possible. Table I shows compound formulations. The stocks were designed for analysis

TABLE I
COMPOUND FORMULAS

Ingredient	C-80-R	C-81-R	C-82-R	C-83-R	C-84-R	C-85-R
Perbunan	100	100
Hycar OR-15	100
Hycar OR-25	100
Neoprene-FR	100	...
Neoprene-GN	100
Benzothiazyl disulfide	1.5	1.5	1.5	1.5
Zinc oxide	3	3	3	3	...	5
Thermax (therma- tomic carbon)	30	30	30	30	30	30
Plasticizer-SC	30	...	30	30	30	30
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5	1	...
Litharge	10	10
Curing time at 308° F	20	20	20	20	30	30

of inherent freeze resistance of the synthetic bases, and are not necessarily practical stocks.

Fuels.—The selection of fuels was based on reports of actual and anticipated use in the field. Type-A gasoline contains cumene as a blending agent. Constants and sources of fuel are presented in Table II. Information available

TABLE II
ANALYSIS OF GASOLINES

Gasoline	Distn. range (° F)	Gum content (mg. per 100 cc.)	Sulfur tarnish on Cu strip	Aniline point (° F)
Technical isooctane	206-238	None	None	175.6
Houdry aviation	118-312	1.6	None	70.7
Type A	300-419	17	None	Below -4
80-octane tank	112-370	19.4	None	97.7
40% aromatics (20% toluene, 15% xylene, 5% benzene)+ 60% technical isooctane	204-290	12.1	Slight	86.7

was limited, and no detailed study was made to correlate composition and specific action on synthetic stocks.

EXTRACTION IN AIR

Figure 2, graph 1, represents the stiffness of the various stocks plotted against decreasing temperature. No gasoline extraction was made. The last

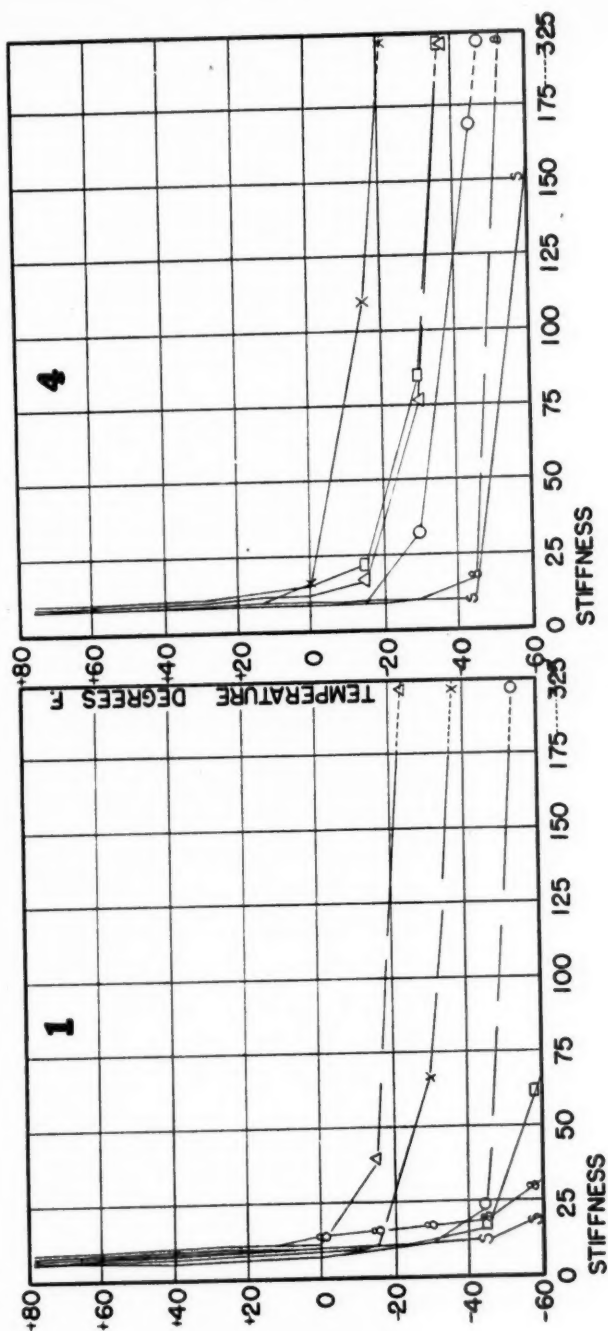


Fig. 2.—Temperature-stiffness curves in air.

1. Original materials, not extracted, cooled in air.
4. Extracted 168 hours at 170° F in Houdry fuel, cooled in air.
- Plasticized Perbunan.
 Δ Unplasticized Perbunan.
 X Plasticized Hycar OR-15.
- Plasticized Hycar OR-25.
 S Plasticized Neoprene-FR.
 8 Plasticized Neoprene-GN.

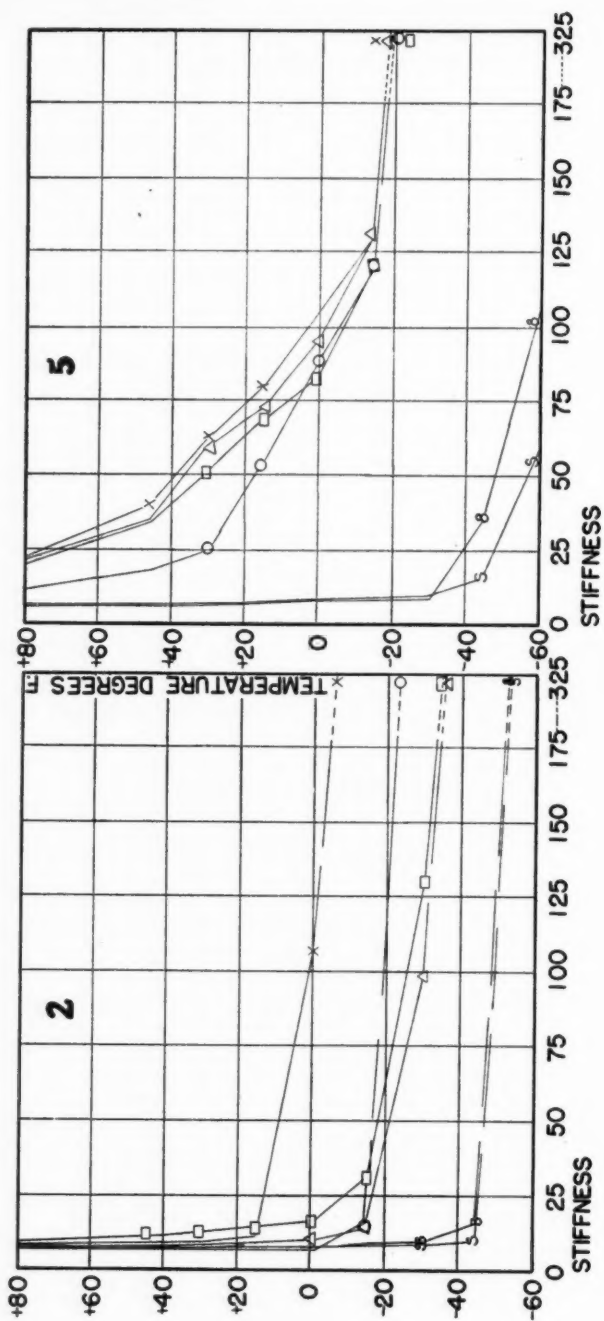


FIG. 2.—Continued.

2. Extracted 168 hours in isooctane, cooled in air.

5. Extracted 168 hours in 80-octane fuel, cooled in air to test-temperature.

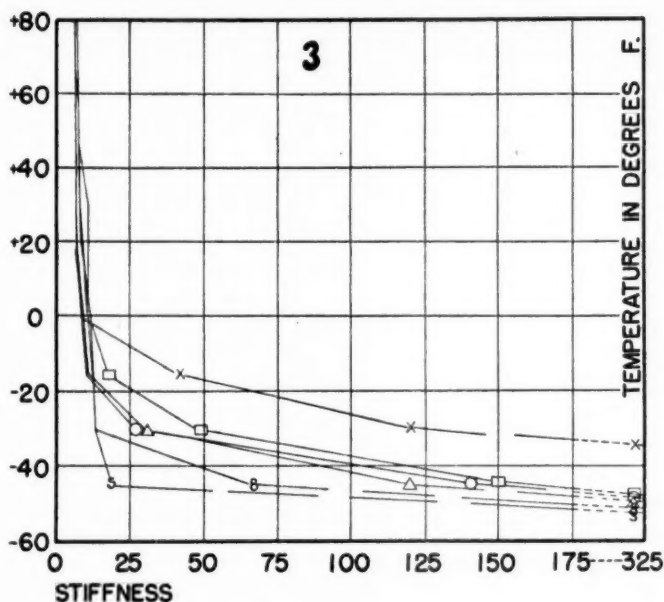


FIG. 2.—Continued.

3. Extracted 168 hours at 170° F in 40% aromatic fuel, cooled in air.

reading preceding the dotted line indicates the stiffening temperature and, as previously explained, represents the temperature below which the force required to flex the sample was beyond the range of the instrument. Only the Neoprenes and plasticized Perbunan stocks are flexible at -60° F, Hycar OR-25 is inflexible at -45°, OR-15 at -30°, and unplasticized Perbunan at -15° F. These curves illustrate inherent freeze resistance of the base synthetics investigated.

The stocks were extracted 168 hours in isooctane, followed by a 15-minute drying period at 180° F in an air oven. During testing they were immersed in air. The stiffening points (Figure 2, graph 2) indicate that compound change has been significantly great. The Neoprenes have a stiffening point 15° F higher than the original compounds unextracted, and the Perbunan and Hycar stiffen at a temperature 30° higher. After extraction the plasticized and unplasticized Perbunan stocks stiffen at approximately the same temperature. It is obvious, then, that plasticization, employed to secure low-temperature flexibility, is without value after stocks have been immersed in isooctane fuel.

Graph 3, Figure 2, shows the effect of immersion in 40% aromatic fuel. Samples were extracted 168 hours, dried, and immersed in air for testing. The general characteristics of the curves indicate rises in stiffening point temperatures compared to the original unextracted samples. The points are lower, however, than in samples similarly extracted in isooctane. The apparent explanation is solvent retention despite a drying period of 15 minutes at 180° F.

Graphs 4 and 5, Figure 2, compare the effect of Houdry fuel and 80-octane

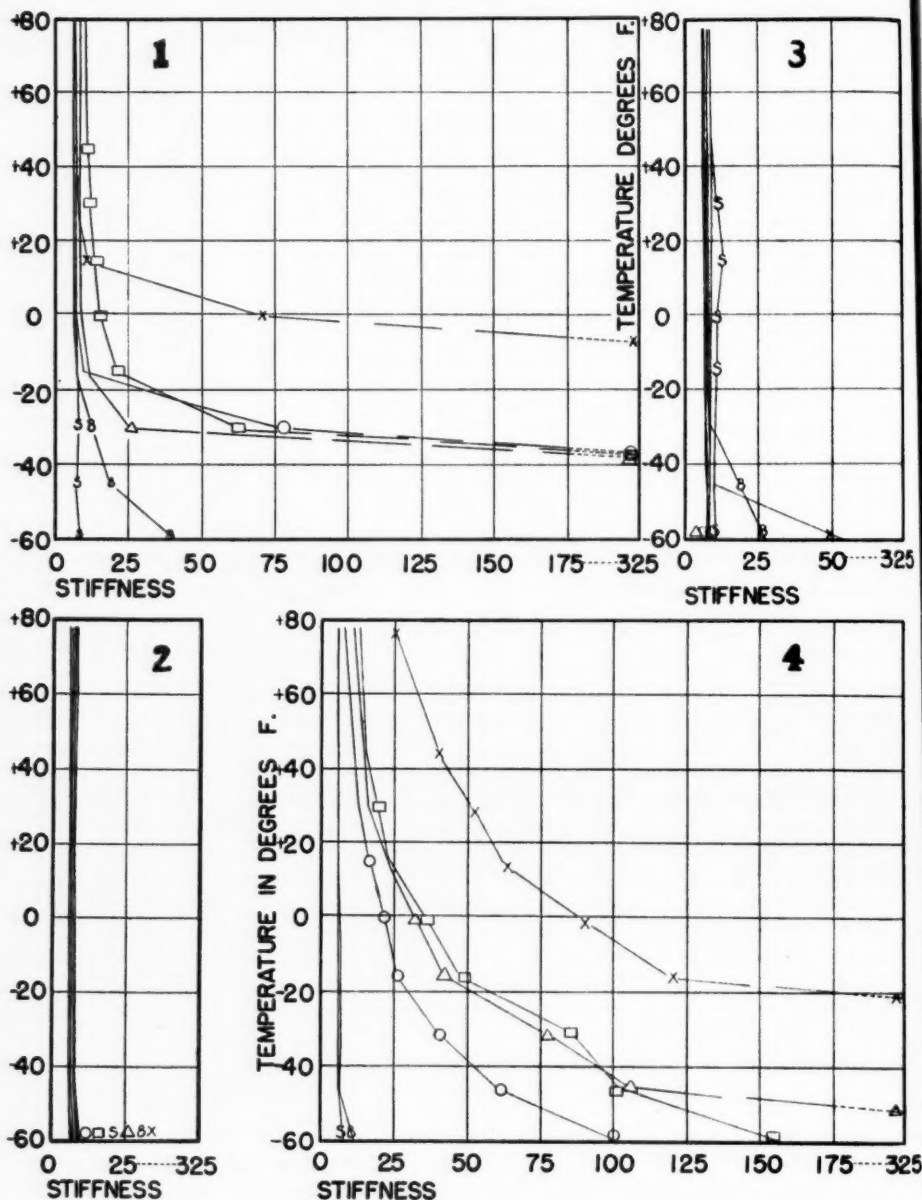


FIG. 3.—Temperature-stiffness curves in fuels.

1. Extracted 168 hours at 170° F in isoctane, cooled in isoctane.
 2. Extracted 168 hours at 170° F in 40% aromatic fuel, cooled in aromatic fuel.
 3. Extracted 168 hours at 170° F in Houdry fuel, cooled in Houdry fuel.
 4. Extracted 168 hours at 170° F in 80-octane gasoline, cooled in 80-octane gasoline.
- Plasticized Perbunan.
 Δ Unplasticized Perbunan.
 X Plasticized Hycar OR-15.
 ○ Plasticized Hycar OR-25.
 S Plasticized Neoprene-FR.
 8 Plasticized Neoprene-GN.

gasoline after immersion for 168 hours. All compounds were again immersed in air during the tests. When compared to the original unextracted curves, a marked increase in stiffening point is observed, due to leaching of plasticizer.

Another significant point is illustrated in the curves of samples immersed in 80-octane gasoline. Aside from a rise in stiffening point, a general increased stiffening occurred throughout the temperature range. The explanation is apparently a specific chemical reaction between the gasoline and synthetic compound. As a matter of fact, type-A fuel stiffened the samples during extraction to such an extent that no flexibility could be secured without fracture.

EXTRACTION IN FUELS

Figure 3 was obtained from samples extracted for 168 hours in the various fuels and then immersed in the same type of fuel during testing.

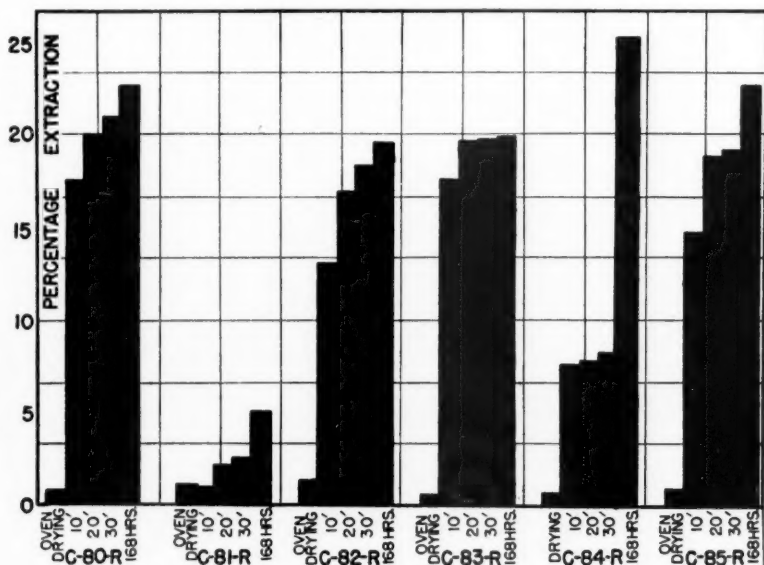


Fig. 4.—Extraction losses in aromatic gasoline.

In the isoöctane gasoline the stiffening points of Neoprene FR and GN were below -60°F , an indication of definite solvent plasticization. The Perbunans and Hycars, however, being more resistant to solvent imbibition, showed no depressing of the stiffening point due to fuel immersion. These data indicate that Perbunan or Hycar compounds designed for low-temperature application might not possess necessary flexibility at -60°F following fuel immersion and extraction, although they might be initially plasticized to meet such service requirements.

Graph 2, Figure 3, representing compounds extracted in 40% aromatic fuel and immersed in the same fuel during test, illustrates a significant point. All the synthetics investigated were plasticized by this fuel, and lost no apparent flexibility even at -60°F . Thus, the type of gasoline used as immersion

media may exert a specific action on the synthetic compounds and provide low-temperature flexibility, even in the absence of usual plasticizers.

Similar plasticizing action on all compounds is observed in graph 3, where Houdry fuel is the immersion media. Likewise, 80-octane fuel functions as a plasticizer and induces flexibility at low temperature in all compounds. Graph 4 shows the plotted data and here, as in graph 5 of Figure 2, there is a general stiffening throughout the temperature range, suggesting chemical action by the fuel on Hycar and Perbunan compounds.

EFFECT OF GASOLINE IMMERSION

To illustrate the rapidity with which plasticizer leaching is accomplished, tests were conducted by extracting each compound in 40% aromatic fuel for

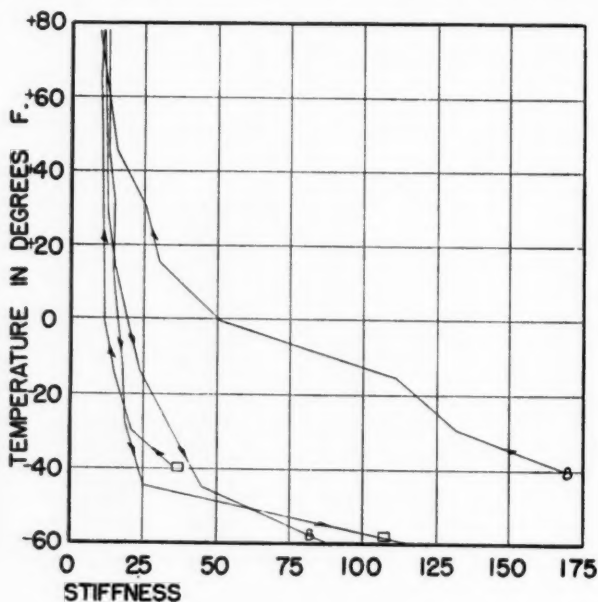


FIG. 5.—Results of 40-hour cold aging.
 □ Plasticized Perbunan. ○ Plasticized Neoprene-GN. ↓ No aging; ↑ after aging.

varying periods. Samples were immersed in the gasoline at 180° F, and swirled in an open-mesh basket for 10, 30, and 60-minute periods. Percentage weight loss was calculated after drying at 180° F in an air oven.

There is no doubt that plasticizer leaching is rapid, especially at the test temperature. Figure 4 shows that in 10 minutes all plasticized stocks lost approximately 80 per cent of their total plasticizer, which was only slightly less than the loss in similar samples extracted 168 hours.

EXTENDED COLD AGING

Various reports have indicated that not all synthetics behave similarly when conditioned at low temperatures for long periods. The tensiometer has confirmed the belief that, at least as far as Perbunan and Neoprene bases are

concerned, resistances to cold are quite dissimilar. Curves (Figure 5) were obtained for plasticized Perbunan and Neoprene-GN according to the standard tensiometer technique, consuming approximately 3 hours. The same samples were then conditioned 40 hours at -40°F , and the stiffness was measured at this temperature. Perbunan lost little of its original flexibility, whereas Neoprene stiffened to more than 400 per cent of its original flexibility. These curves were made with the samples immersed in air. We have not at this time conducted a more comprehensive investigation of the effect of different low temperatures or different aging periods, nor have we conditioned samples immersed in gasolines. Evidence indicates, however, that those testing methods designed to measure freeze resistance and low-temperature flexibility of various synthetic stocks must be capable of estimating the effect of prolonged cold aging.

SUMMARY

A tensiometer can be used to measure the stiffness of rubber stocks; accurate data are secured which lend themselves to a quantitative interpretation of the effect of low temperatures on any compound. Where changes in the sensitivity to flexing of thin rubber sections are important, such data, represented by curves of temperature *vs.* flexibility, seem more important than durometer changes and bend-brittle points. The compounding practice of high plasticizer does not in itself provide low-temperature flexibility where fuel immersion and ensuing plasticizer extraction are conditions of service. Tests designed to evaluate low-temperature flexibility and freeze resistance which utilize organic liquids as temperature conditioners must be double-checked to ensure that the cooling medium is not exerting its own specific effect on the stocks. Graphs indicate the influence of aviation fuels on low-temperature resistance; it has been experimentally proved by the same method that acetone has a similar effect. It is established that some synthetics are more resistant than others to prolonged low temperature. Service requirements and field conditions should be carefully considered in all cases where laboratory evaluation does not include every variable factor. The need for a thorough application analysis of functional stocks cannot be overemphasized.

A LOW-TEMPERATURE STIFFNESS TEST FOR ELASTOMERS*

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Most synthetic vulcanizates stiffen more than natural vulcanizates at low temperatures. This behavior has aroused considerable interest in the development of suitable tests for the cold resistance of synthetic vulcanizates. Inasmuch as all rubbers gradually stiffen and finally become brittle as the temperature is lowered, two general types of cold resistance tests have been developed, *viz.*, stiffness tests and brittleness tests. The stiffness tests involve a quantitative measurement of the resistance to deformation of the specimens; the brittleness tests consist in determining the temperature at which the specimens will fracture when rapidly bent. We are concerned here only with stiffness testing.

PREVIOUS STIFFNESS TESTS

Most low-temperature stiffness tests which have been devised determine the flexural properties of the specimens. This is the case with the tests developed by Koch¹, McCortney and Hendrick², Kish³, Werkenthin⁴, Green, Chollar, and Wilson⁵, and Liska⁶. The remainder of the stiffness tests apply stress to the specimen in other ways. Yertzley and Fraser⁷ developed a torsion test and a Shore durometer test. Clash and Berg⁸ described a torsion test. Russell⁹, Graves and Davis¹⁰, and Buckley and Chaney¹¹ proposed tensile tests.

ADVANTAGES OF NEW METHOD

In view of the considerable number of cold-stiffness tests which have been suggested, the presentation of yet another stiffness test requires justification. This can best be done by pointing out the advantages of the new test for development and specification work. The following advantages are claimed for the new test:

1. Set may be determined as well as stiffness.
2. The test-specimens are very small, and can be prepared readily from almost all rubber goods.
3. Air is used as the cold transfer medium instead of alcohol, which swells some elastomers.
4. The cold-generating apparatus can be relatively simple and can be built from inexpensive materials, or it can be purchased commercially.
5. The stiffness-measuring apparatus is simply constructed, and its manipulation is very easy.
6. The stiffness-measuring apparatus employs a weight for application of load to the test-specimen instead of a spring. Therefore there is no need of frequent calibration, as when a spring is employed.
7. The precision of the method is believed to be at least as high as the precision of the other cold-stiffness tests.

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DESCRIPTION OF NEW LOW-TEMPERATURE STIFFNESS TEST

The new test consists of stretching a small specimen in cold air by means of a definite load acting vertically and measuring the elongation obtained. The less is the elongation under load, the stiffer is the stock. Set is determined by removing the load and observing the recovery of the specimen after a given time.

The test-specimen is the ordinary T-50 specimen shown in Figure 1. The thickness of the specimen is optional. The thickness used in most of the tests

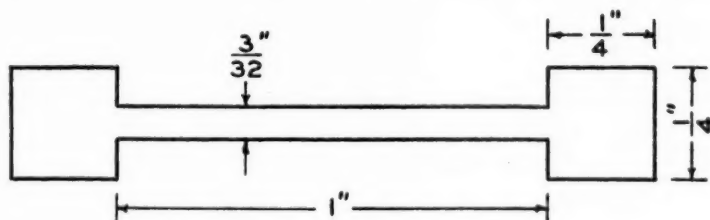


FIG. 1.—Test-specimen.

reported herein was $\frac{1}{16}$ inch. This small specimen can be prepared conveniently from almost all types of rubber goods, using the die manufactured by Henry L. Scott Co. The clamps for holding the specimen during test can also be obtained from this company.

Inasmuch as the test involves measuring deflection under a constant load, it is imperative that the load per cross-sectional area be maintained absolutely uniform from one specimen to the next specimen, notwithstanding possible variations in width and thickness of the specimens. Thus it is necessary to select some load per cross-sectional area as standard, and adjust the actual stretching weight to conform with this value. In this work it was decided to standardize on three loads, 256, 512, and 1024 lbs. per sq. in. These loads correspond to stretching weights of 1.5, 3 and 6 pounds, respectively, acting on a specimen having a cross-section of $\frac{1}{16}$ inch by $\frac{3}{32}$ inch. In specification work it may be desirable to employ other loads, depending on the type of vulcanizate under consideration.

It is important that the specimens shall have a uniform cross-section along their restricted portion. The variation in width or thickness must not exceed 0.002 inch if precise results are desired. The authors have experienced no trouble in preparing samples to this tolerance. The T-50 specimens were died out after buffing. The Bausch & Lomb measuring microscope, with 20-millimeter scale divided in 0.1 millimeter divisions, is a convenient and inexpensive device for measuring accurately the width of the specimens.

The upper and lower clamps which hold the specimen during test are shown in Figure 2. The rod attached to the lower clamp holds the weight by means of the hook on its lower end. A scratch on the rod serves as an index to enable the elongation of the specimen to be measured outside of the cold box by means of a steel ruler, which is divided in hundredths of an inch. The combined weight of the lower clamp and rod is only 0.04-pound and may therefore be neglected. The thermal elongation of the rod due to being pulled out of the cold box by the weight is also negligible.

A convenient weight for this test is a metal cup containing fine lead shot

and provided with a wire loop for attaching to the hook on the rod. This weight can be readily adjusted to obtain the desired load per cross-sectional area of the specimen.

The positions of the clamps, the specimens, and the rods in the cold box are illustrated in Figure 3. The rods pass through $\frac{1}{4}$ -inch holes in the bottom

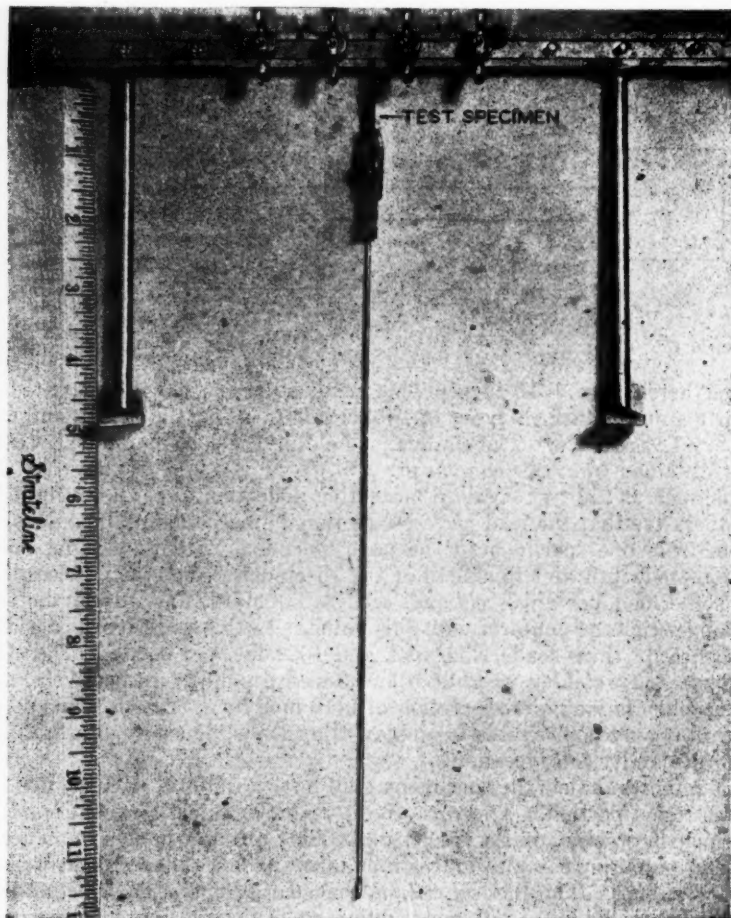


FIG. 2.—Test-specimen in clamps with measuring rod on lower clamp.

of the cold box. These holes are closed by lightly stuffing cotton alongside the rods except at the time of measurement.

It should be understood that a cold box with a glass front is not required for this test, since it is not necessary to see the specimens during test. The cold box, however, must be arranged for good circulation of air.

The authors employed a special apparatus (Figure 4) for blowing cold air at constant temperature into the cold box. This apparatus is made by Tenney

Engineering, Inc., and is called "packaged air". This apparatus is provided with outlet and return ducts for connection with any box in which it is desired to maintain constant temperature. The outlet and return ducts of the "packaged air" apparatus were connected to the cold box used in this investigation by means of the rubber ducts shown in Figure 5. A baffle was placed in the end of the outlet duct to prevent the cold air from blowing directly on the specimens.

The "packaged air" apparatus is charged with dry ice. By means of a blower the air from the return duct is drawn over electric strip heaters or bypassed by a damper valve through dry ice before being blown through the

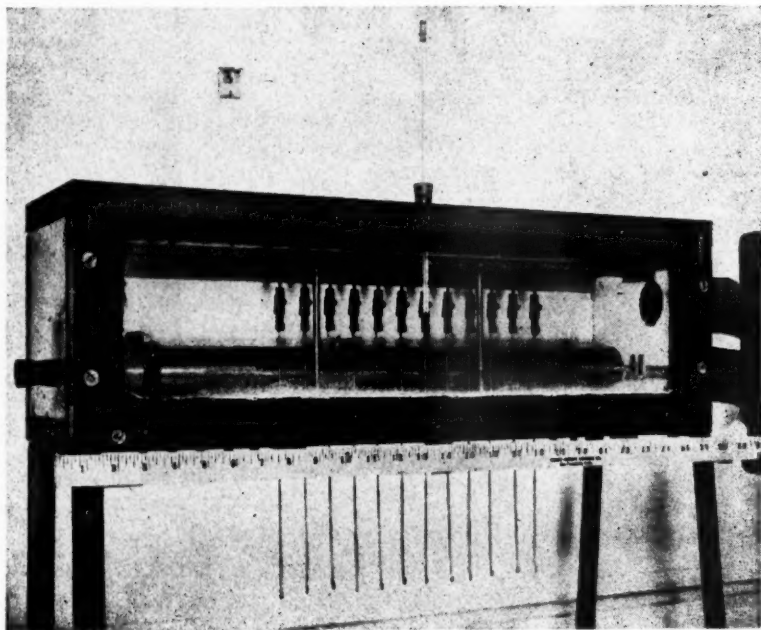


FIG. 3.—Cold box containing clamped specimens.

outlet duct. The temperature of the air is controlled within plus or minus 1°C by a thermoregulator, which operates the electric strip heaters and the damper valve.

The "packaged air" apparatus is a convenient source of constant-temperature cold air, but a less-elaborate source of cold air can be used for the stiffness test. A simpler apparatus which has been found suitable is diagramed in Figure 6. This apparatus can be built from parts to be found in most laboratories. It combines the cold generation and testing in one box.

Preliminary experiments with specimens prepared from a Hycar OR-15 stock (Table 1) showed that the conditioning period should be two hours before stretching, and the time of reading the elongation should be three minutes after hanging on the weight. These intervals were adopted as standard.

PRECISION OF TESTS

It is important that all testing methods for rubbers shall have a fair degree of precision. In other words the results shall be reproducible. The precision of the proposed stiffness test was determined by conducting numerous tests at each of several temperatures on the *Hevea* stock, the plasticized Perbunan-26 stock, and the plasticized Hycar OR-15 stock formulated in Table 1, and two

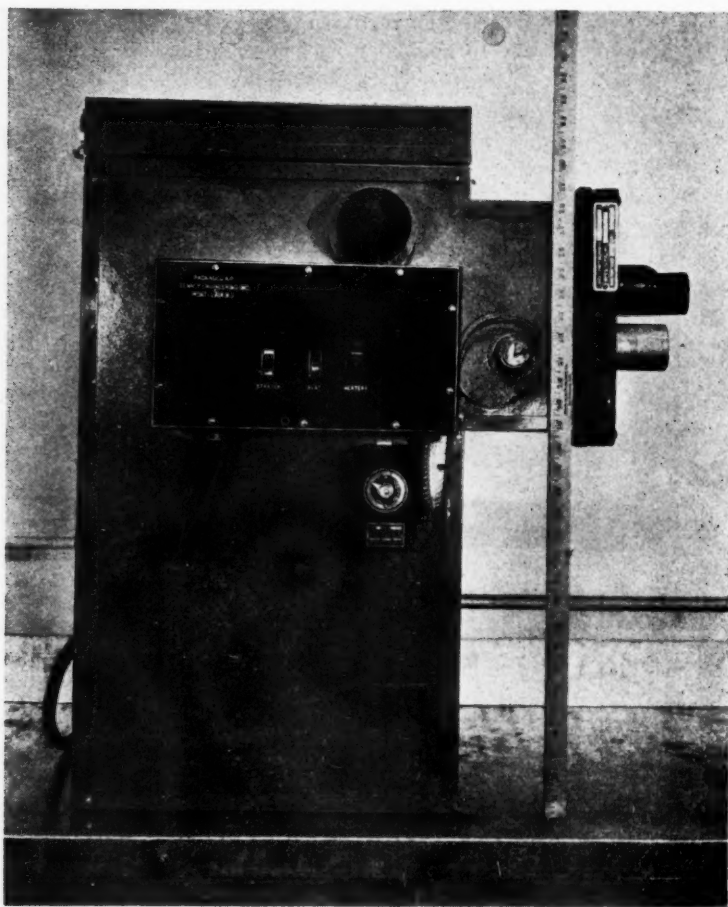


FIG. 4.—"Packaged air" apparatus.

commercial Neoprene hose cover stocks and then analyzing the data from each series of tests on the same compound, tested under different conditions by determining the standard deviation and percentage standard deviation for each series. The standard deviation, which may be stated to be the root-mean-square deviation of a group of numbers from their average, under these conditions specifically defines the range on either side of the mean value

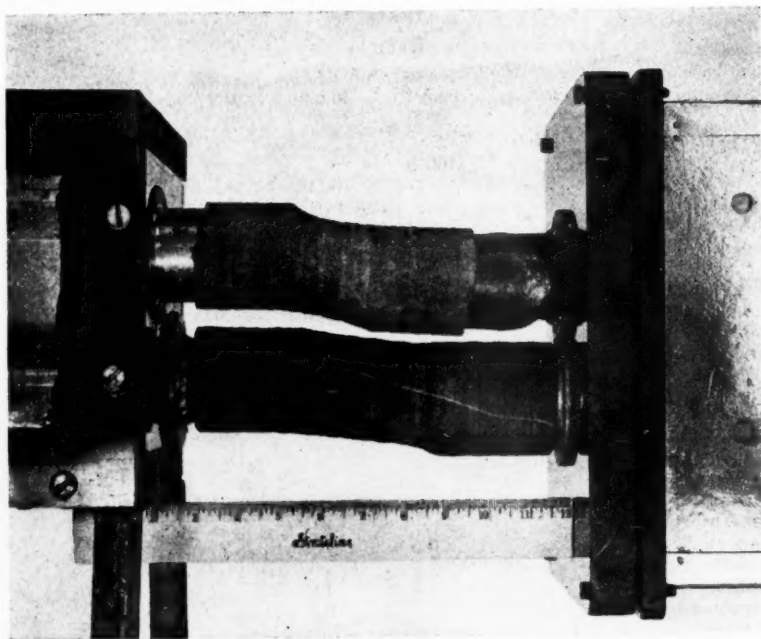


Fig. 5.—Rubber ducts for circulation of cold air between "packaged air" apparatus and box.

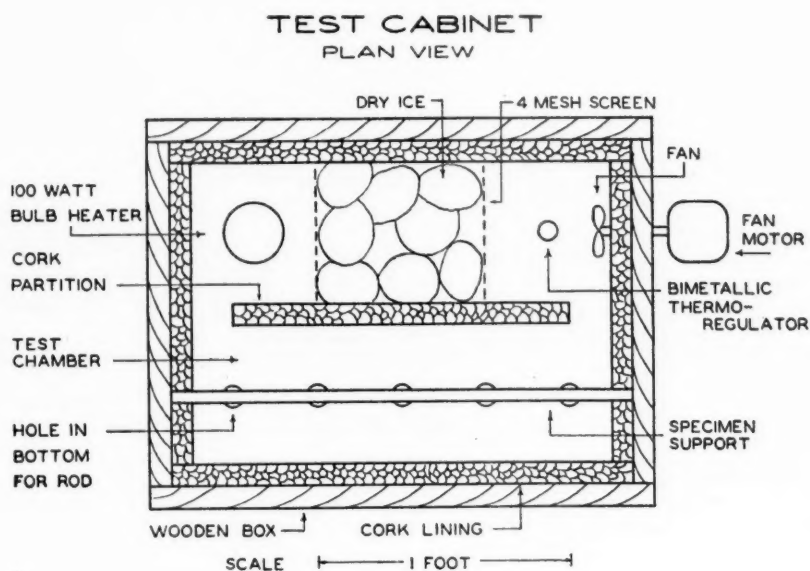


Fig. 6.—Optional apparatus for low-temperature stiffness test.

TABLE I
RECIPES

	Hevea stock	Buna-S stock	Butyl stock	Neoprene- GN stock	Neoprene- FR stock	Thiokol-FA stock
Smoked sheet.....	100.0
GR-S.....	...	100.0
GR-I.....	100.0
Neoprene-GN.....	100.0
Neoprene-FR.....	100.0	...
Thiokol-FA.....	100.0
SRF black (40 volumes)	78.3	76.6	78.2	58.5	63.2	54.1
Zinc oxide.....	5.0	5.0	5.0	5.0	...	10.0
Light magnesia.....	4.0
Litharge.....	10.0	...
Stearic acid.....	2.0	...	1.0	0.5	1.0	0.5
Phenyl- α -naphthyl- amine.....	1.0	1.0	...	2.0	2.0	...
Diphenylguanidine.....	0.1
Benzothiazyl disulfide..	0.8	0.3
Zinc dimethyldithio- carbamate.....	0.1
Tetramethylthiuram monosulfide.....	...	0.5
Tetramethylthiuram disulfide.....	1.0
Mercaptobenzothiazole..	0.5
Sulfur.....	2.5	2.0	1.5	...	1.0	...
	Perbunan- 26 stock	Plasticized Perbunan- 26 stock	Hycar OR-15 stock	Plasticized Hycar OR-15 stock	Neoprene- ILS stock	Plasticized Neoprene- ILS stock
Perbunan-26.....	100.0	100.0
Hycar OR-15.....	100.0	100.0
Neoprene-ILS.....	100.0	100.0
SRF black (40 volumes)	74.2	74.2	72.0	72.0	58.1	58.1
Zinc oxide.....	5.0	5.0	5.0	5.0	10.0	10.0
Light magnesia.....	10.0	10.0
Stearic acid.....	1.0	1.0	1.0	1.0	0.5	0.5
Dibutyl phthalate (10 volumes).....	...	10.7	...	10.5	...	8.5
Dibutyl sebacate (10 volumes).....	...	9.6	...	9.3	...	7.5
Tributoxyethyl phos- phate (10 volumes)..	...	11.5	...	11.1	...	9.0
Phenyl- α -naphthyla- mine.....	1.0	1.0	1.0	1.0	2.0	2.0
Benzothiazyl disulfide..	1.75	1.75	1.75	1.75
Di- <i>o</i> -tolylguanidine salt of dicatchol borate..	1.0	1.0
Sulfur.....	1.75	1.75	1.75	1.75

within which two-thirds of the test values may be expected to fall. Therefore the smaller the standard deviation, the more dense the clustering and the

greater the indicated precision. The percentage standard deviation or coefficient of variation, which is the standard deviation divided by the arithmetical mean multiplied by 100, is used to compare the relative variability of two or more series of tests, since in these tests, as mentioned below, the standard deviation remains about the same as the temperature is lowered, while the elongation decreases.

In the case of the *Hevea* and plasticized Hycar OR-15 stock, tests were performed on specimens which had been died out with the grain and also on specimens which had been died out radially. Some of the radially died specimens were with the grain; some were across the grain, and some were intermediate. The Perbunan-26 stock was tested at three different specimen thicknesses. All specimens were died out with the grain. The Neoprene hose-cover specimens were all died out in the same direction, but it is not known whether these were with the grain or across the grain.

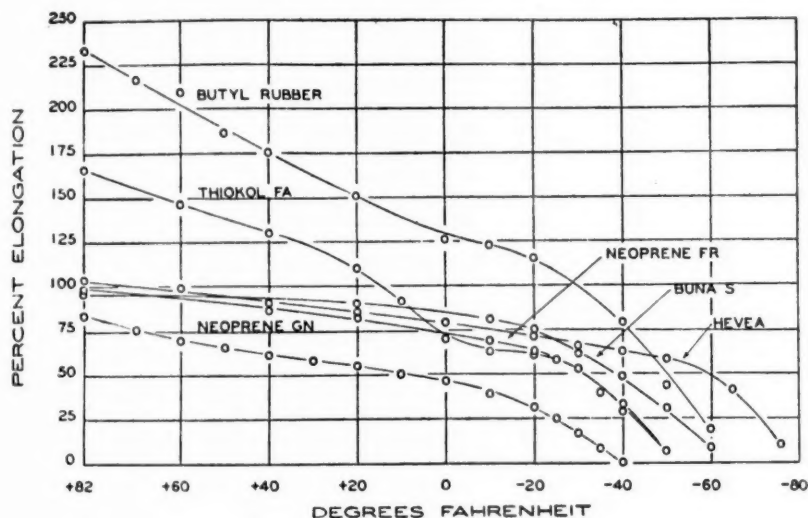


Fig. 7.—Relation between elongation at 512 lbs. per sq. in. load and temperature

The statistical data, presented in Table 2, show that the proposed stiffness test yields quite reproducible results. Greater precision is obtained by dieing out the specimens in the same direction instead of radially because of the grain effect. The precision of the test, measured by the percentage standard deviation, generally decreases as the temperature is lowered because the actual magnitude of the standard deviation remains approximately the same although the elongation decreases. Changing the thickness of the specimens, but keeping the load constant per cross-sectional area does not alter significantly the results of the stiffness test or the precision of these results.

The precision of the set measurements of the plasticized Perbunan-26 stocks has determined at -20°F , in conjunction with the above-mentioned stiffness tests. The set measurements were made 5, 10, 15, and 60 seconds after removal of the stretching weight (512 lbs. per sq. in. load), which had acted on the specimen for exactly three minutes. The set test is not so precise as the stiffness test.

TABLE 2
STATISTICAL DATA ON STIFFNESS TESTS

Stock	Temperature of test (° F)	Number of observations (load = 512 lbs. per sq. in.)	Thickness of specimens (inch)	Highest elongation in group (%)	Lowest elongation in group (%)	Average elongation in group (%)	Standard deviation	% Standard deviation
<i>Hevea</i> *	+82	24	0.0625	98	90	94	2.2	2.4
	0	24	0.0625	75	68	73	1.5	2.0
	-30	24	0.0625	70	64	66	1.7	2.5
	-60	23	0.0625	53	43	48	2.7	5.7
<i>Hevea</i> †	+82	24	0.0625	113	103	107	2.5	2.4
	0	24	0.0625	86	77	81	2.4	2.9
	-30	24	0.0625	81	64	71	4.5	6.3
	-60	24	0.0625	54	41	48	3.2	6.6
Plasticized Perbunan-26*	-20	23	0.040	137	125	131	3.4	2.6
	-20	24	0.060	139	121	132	4.0	3.0
	-20	21	0.080	145	128	134	4.6	3.4
Plasticized Hycar OR-15*	+82	24	0.0625	172	160	167	2.9	1.7
	0	24	0.0625	126	109	117	4.8	4.1
	-30	24	0.0625	31	19	25	3.4	13.6
Plasticized Hycar OR-15*	+82	24	0.0625	186	158	171	9.0	5.3
	0	24	0.0625	141	110	120	8.0	6.7
	-30	24	0.0625	33	15	24	5.9	24.7
#1 Neoprene hose cover*	0	24	0.0625	122	102	112	5.7	5.1
	-20	24	0.0625	92	77	86	4.0	4.6
#2 Neoprene hose cover*	0	23	0.0625	58	49	53	2.2	4.2
	-20	24	0.0625	34	25	31	2.6	8.2

* Specimens died out in the same direction

† Specimens died out radially

TABLE 3
STATISTICAL DATA ON SET TESTS—PLASTICIZED PERBUNAN STOCK AT -20° F

Test	Number of observations	Highest value in group (%)	Lowest value in group (%)	Average value in group (%)	Standard deviation	% Standard deviation
Thickness of specimens = 0.040-inch						
Elongation with 512 lbs. per sq. in. load.....	23	137	125	131	3.4	2.6
Set at 5 seconds.....	23	36	19	26	4.8	18.5
10 seconds.....	23	27	14	19	3.6	19.1
15 seconds.....	23	22	11	15	3.0	19.9
60 seconds.....	23	12	7	9	1.8	19.5
Thickness of specimens = 0.060-inch						
Elongation with 512 lbs. per sq. in. load.....	24	139	121	132	4.0	3.0
Set at 5 seconds.....	24	30	20	25	2.9	11.5
10 seconds.....	24	22	15	18	2.1	11.9
15 seconds.....	24	19	12	15	2.0	13.0
60 seconds.....	24	13	8	10	1.4	14.3
Thickness of specimens = 0.080-inch						
Elongation with 512 lbs. per sq. in. load.....	21	145	128	134	4.6	3.4
Set at 5 seconds.....	21	27	15	21	3.7	17.6
10 seconds.....	21	21	9	15	2.8	18.5
15 seconds.....	21	19	7	13	2.7	20.4
60 seconds.....	21	15	5	8	2.1	26.8

RESULTS OBTAINED

Stiffness data for the *Hevea* stock and some synthetic stocks are plotted versus temperature in Figures 7 and 8. Each point in these graphs is the

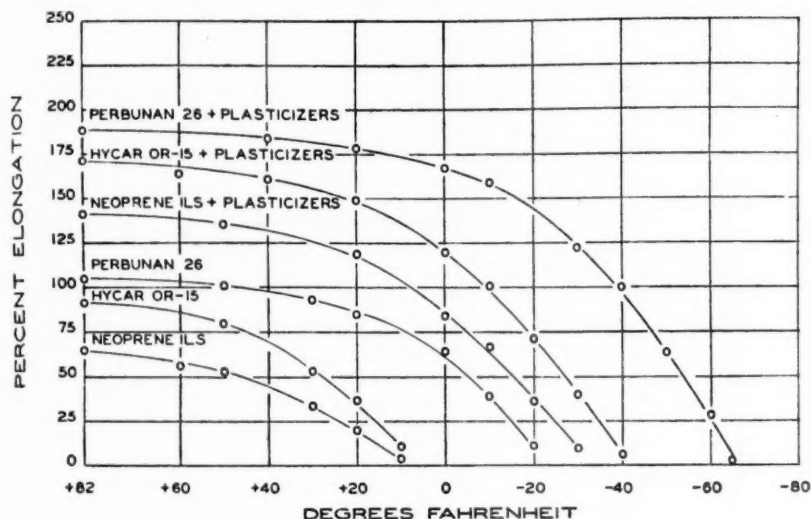


Fig. 8.—Relation between elongation at 512 lbs. per sq. in. load and temperature

average of six determinations. The recipes and certain physical properties of these stocks are given in Tables 1 and 4, respectively. All of the stocks contain the same volume of semireinforcing furnace black, and the plasticized stocks contain the same volume of plasticizers.

TABLE 4
CURES AND PHYSICAL PROPERTIES

Stock	Cure	Tensile strength lbs. per sq. in.	Ultimate elongation (%)	Modulus at 200% elongation	Shore hardness (10 seconds on $\frac{1}{4}$ -inch)
<i>Hevea</i>	20 min. @ 260° F	3070	450	1600	65
Buna-S.....	20 min. @ 287° F	1900	200	1900	66
Butyl.....	150 min. @ 307° F	1200	390	910	65
Neoprene-GN.....	40 min. @ 287° F	2760	300	2190	73
Neoprene-FR.....	40 min. @ 287° F	2240	200	2240	65
Thiokol-FA.....	40 min. @ 298° F	1300	400	850	61
Perbunan-26.....	60 min. @ 274° F	2730	300	1920	64
Plasticized Perbunan-26	60 min. @ 274° F	1700	390	800	46
Hycar OR-15.....	60 min. @ 274° F	2810	320	2260	69
Plasticized Hycar OR-15	60 min. @ 274° F	2180	500	960	50
Neoprene-ILS.....	40 min. @ 307° F	2980	200	2980	75
Plasticized Neoprene-ILS	40 min. @ 307° F	1970	270	1370	58

All of the stocks except the Butyl and Thiokol-FA stocks exhibited the same type of stiffness-temperature curve. The latter stocks gave a very high elongation at room temperature, and the elongation decreased rapidly as the temperature decreased. Both curves possessed a slight inflection at about

-10° F. The curves for the *Hevea*, Buna-S, and Neoprene-FR stocks were quite similar down to about -20° F. Below this temperature the *Hevea* stock was the most flexible, and the Neoprene-FR stock was the least flexible. The addition of plasticizers to the Perbunan-26, Hycar OR-15, and Neoprene-ILS stocks enhanced their flexibility at room temperature and at lower temperatures.

The elongations and sets at -20° F of the *Hevea*, plasticized Perbunan-26, plasticized Hycar OR-15, and plasticized Neoprene-ILS stocks are graphed in Figure 9. The low set of the plasticized Perbunan-26 stock is noteworthy.

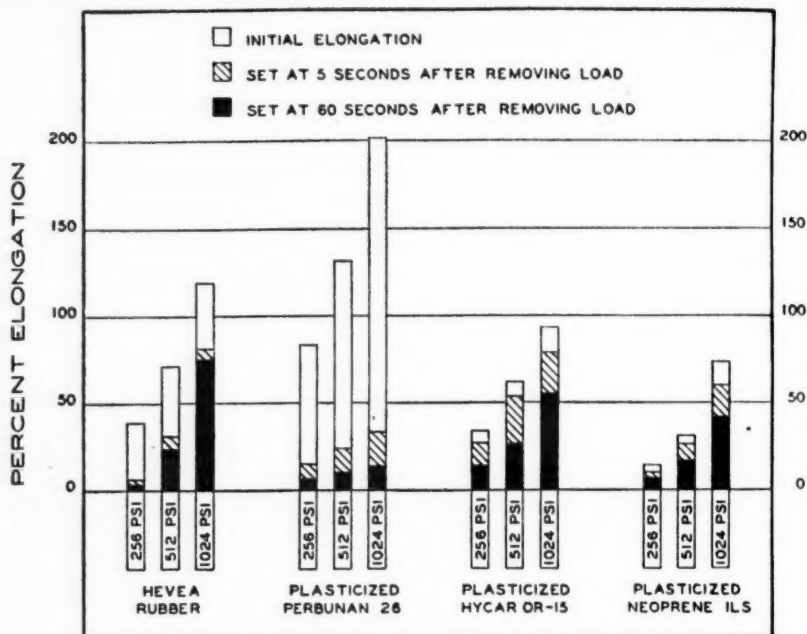


FIG. 9.—Elongations at various loads and corresponding sets, all at -20° Fahrenheit

FURTHER ADVANTAGES

The usefulness of the proposed stiffness test is not limited to determining the effect of low temperature; it may also be used to characterize a stock at room temperature. Like the Shore hardness test, the stiffness test requires relatively inexpensive and uncomplicated equipment. It has the advantage over the Shore hardness test of being more precise, although it is less convenient. An example of where the stiffness test should find application is in the determination of the rate of cure of small, thin moulded items on which a reliable Shore hardness test or regular tensile test cannot be made. Another example is in the determination of plastic flow under constant stress at high temperatures.

ACKNOWLEDGMENT

The authors wish to express appreciation for the assistance of Harold N. Olsen in constructing some of the apparatus used in this study.

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A SIMPLIFIED HOT TENSILE TEST FOR GR-S*

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In September, 1942, the hot-iron test developed by E. Valden, of these laboratories, was demonstrated¹ as a simple rapid method of evaluating the heat embrittlement of GR-S. The test-specimen, a T-50 test-piece, may be cut from the remnants of test sheets cured for stress-strain determinations. For GR-S trends a convenient set of conditions is 200 per cent elongation and an iron temperature of 400° F.

The iron is fastened to the test-block at a sufficient height to assure positive contact of the specimen with the iron, and the screws in the spacer blocks are set to give a 200 per cent elongation². The iron, a "patch heater", for spotting or dry-mounting photo prints, has a built-in thermostat. The time in seconds between contact of the specimen with the iron and its failure due to heat is recorded. The relative behavior of various elastomers with 27.8 volumes of carbon is illustrated in Figure 1. The excellence of *Hevea* at both optimum

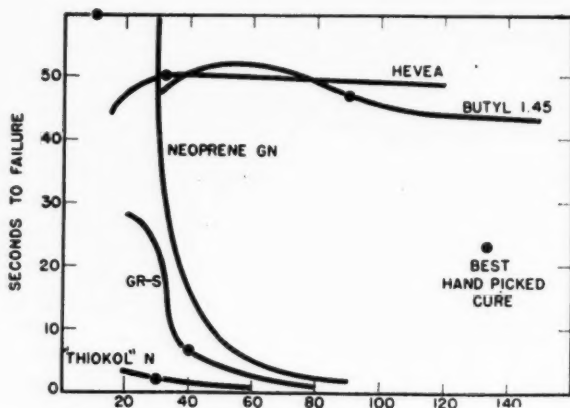


FIG. 1.—Heat failure of various rubbers with 27.8 volumes of carbon black.

and prolonged overcure is apparent. The hot-iron test does not serve to pick best cure. It does provide an effective warning against overcure and a means of recognizing compounding changes which benefit heat stability, as, for example, the use of high carbon high softener ratios³.

The general recognition of the tenderness of hot GR-S has necessitated the emphasis on high-temperature tests for all compounding studies. Few laboratories are equipped with the conventional types of hot tensile testers, and

* Reprinted from the *India Rubber World, Natural and Synthetic*, Vol. 110, No. 6, pages 645-646, September 1944. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in New York City, April 26-28, 1944.

under present restrictions these are almost unobtainable. Improvisations have been developed. A modification of the hot-iron test is possibly one of the simplest of these. As shown in the insert on Figure 2, a slightly crowned groove was cut into the face of the brass heel-piece of the hot iron of sufficient width and depth to take the straight portion of a standard dumbbell test-piece. The heel-piece has a hole drilled parallel to this groove into which a thermocouple needle can be inserted for adjusting and checking the temperature of the iron.

In operation, the test-specimen is mounted in the tensile tester in the standard manner, and the down pull started. The hot iron is then held against

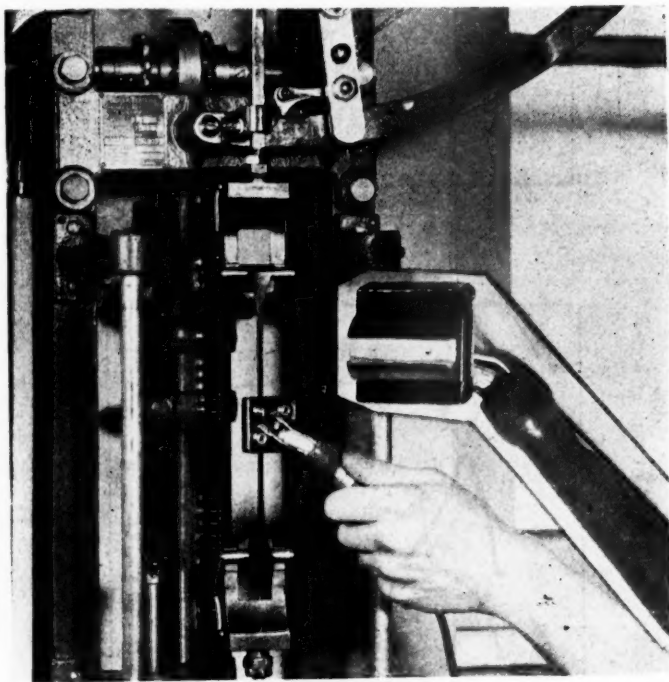
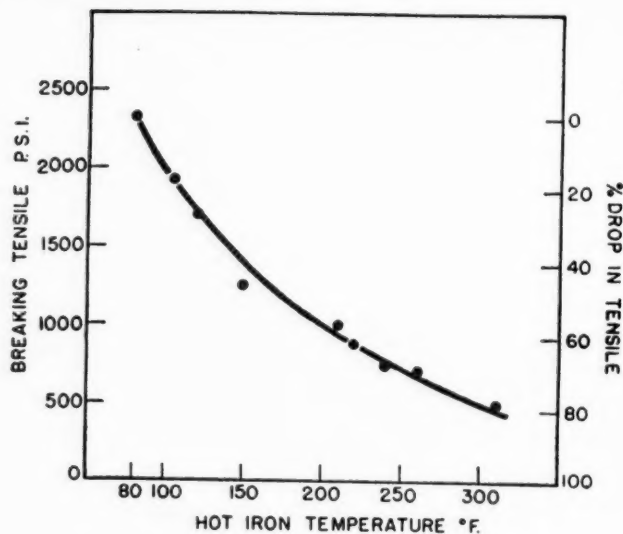
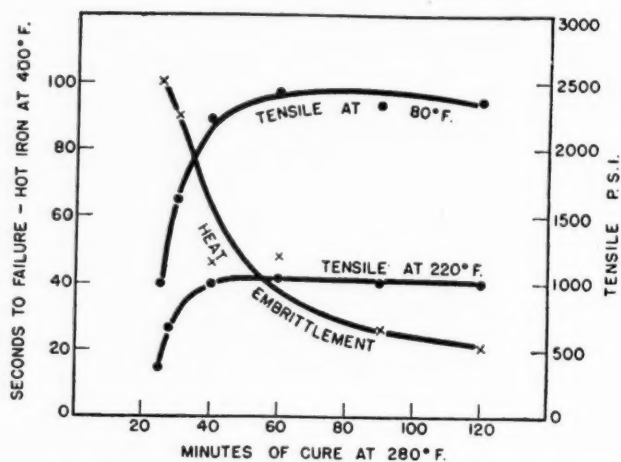


FIG. 2.—Operation of hot-iron tensile test; insert shows groove cut into the iron to take straight portion of test-piece.

the center of the test strip, as shown in Figure 2. As the sample is stretched, the iron is moved down to keep it centered between the standard bench-marks. The effect of iron temperature on the WPB test tread is shown in Figure 3. A temperature of 200 to 220° F produces a tensile drop of about 60 per cent.

To permit comparison between conventional room temperature tensiles and hot tensiles of specimens cut from the same standard test sheet, the dimensions of the A.S.T.M. test-strip die were modified. The end tabs only were shortened, reducing the total length of the specimen by $\frac{5}{8}$ inch, and the width of the end tabs narrowed by $\frac{3}{8}$ inch. This left the length and width of the center portion of the test-piece and the radii to the tabs unaltered, and thus did not change the conventional tensiles from those obtained with the standard test-strip die. By the use of this modified die, ten specimens can be cut from

Fig. 3.—Tensile of GR-S tread compound *vs.* temperature.Fig. 4.—Tensiles at 80° F and 220° F and heat embrittlement *vs.* cure of a GR-S tread.

a standard six-inch by six-inch test sheet as against a maximum of about six with the standard die. This makes it possible to break five test-specimens at room temperature and another five at an elevated temperature, all from a single sheet.

Since hot tensile-testing is frequently done by immersing the specimens into boiling water, a temperature of 220° F was tentatively selected for the hot iron. This excess over the temperature of boiling water was an empirical allowance for the fact that the sample is not immersed into hot liquid. Conditioning the test-piece in a Geer oven at 212° F before determining the hot tensile with the iron showed no significant difference. Using this temperature,

some data have been accumulated on hot tensile *vs.* room temperature tensile. It is not the purpose of this paper to discuss the effect of compounding variables on hot tensile, but Figure 4 shows a typical room temperature tensile, hot tensile, and hot-iron or heat-embrittlement curve for a GR-S tread compound. For this compound best hand-picked cure, namely, the best compromise between snap and tear, comes about ten minutes earlier than maximum room temperature tensile. Hot tensile is also shown to come slightly earlier than maximum room temperature tensile, thus approximating the best cure more closely. This is not universally true. Of 77 compounds tested, 32 cases showed maximum hot tensile at the same cure as maximum room temperature tensile; 33 cases showed earlier; and only 12 cases showed hot tensile later than room temperature tensile. It is thus seen that hot tensile tends to an earlier maximum than room temperature tensile, thus favoring cures with better tear and agreeing more closely with best hand-picked cure as defined above.

Since the specimen is heated by contact with the hot iron, a time factor is introduced. This must be recognized when comparing stocks of different degrees of reinforcement and consequently different modulus, since high-modulus stocks naturally build up considerable stress before the specimen is heated uniformly.

A comparison of results with the high-temperature Scott tester showed very good correlation, and it is believed that a hot iron temperature of 230° F will give hot tensile values for GR-S stocks, agreeing within experimental error with those obtained when the specimen is immersed in boiling water.

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STAINING RUBBER IN GROUND OR MILLED PLANT TISSUES *

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Accessory to a comprehensive study of guayule production now under way by the United States Department of Agriculture is an analysis of the rubber content of plants of various strains and ages grown under diverse environmental conditions. This analysis is currently made by chemical extraction of the rubber from finely ground tissues by a method based on that described by Spence and Caldwell¹. This method consists of a number of distinct steps, and it is part of the program to test possible variants of these steps. As a check on the effectiveness of such tentative modifications, the ground samples are examined microscopically, especially the spent charges remaining after extraction.

RUBBER-STAINING DYES

In the microscopic inspection of tissues, it is common practice to use various dyes for staining diverse plant substances, sometimes singly, sometimes in combination². For staining rubber in plant sections, Lloyd³ used alkanet, while Hall and Goodspeed⁴ and Artschwager⁵ employed Sudan III. Other dyes which stain guayule sections in patterns similar to those of Sudan III are Sudan IV, Sudan black B, and Calco oil blue NA. Unfortunately, these dyes are not specific for rubber, but also stain various other materials, such as resins, oils, fats; suberin, and cutin⁶. Steps must accordingly be taken to eliminate these substances from the sample or to learn to recognize them by some distinctive character of form, color, or location. An experienced microscopist or technician might be expected to recognize the various tissues and substances in plants with which he is working, often without any staining at all⁷. For many workers, however, staining and counterstaining will prove an exceedingly useful aid in studying plant material. It is for this group that these notes are intended.

Suberin can be decomposed by treatment with potassium hydroxide in ethyl alcohol⁸, after which the cork cell walls no longer take up the rubber-staining dye. Any fats that may be present will likewise be saponified by the potassium hydroxide. For getting rid of resins and oils, acetone or ethyl alcohol may be used⁹. Pigments can be bleached out by means of oxidizing agents.

Needless to say, the microscopic examination of ground samples is a far different matter from that of ordinary sections. In the ground material the various structural elements are mostly much displaced from their original relative locations, many of the fragments are thicker than the usual run of sections, and the pieces are sometimes piled one on top of another. The face exposed under the cover-glass of a microscopic mount is usually longitudinal,

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cross-sectional exposures being uncommon. Before extraction, stained rubber agglomerates are likely to be fairly plentiful, especially in the case of plants of high rubber content.

STAINING SCHEDULE

The choice of dye is partly a matter of personal preference. Sudan III colors rubber somewhat scarlet, while Sudan IV gives more of a crimson cast. Sudan black B gives an indigo or dark blue, approaching black, and Calco oil blue NA a much brighter blue. Addicott¹⁰ has recently described a combination dye resulting in a blue staining of the rubber with red coloration of lignified and suberized tissues. In working with ground material of guayule and other plants, the author found that Sudan IV combined with either iodine green or methyl green yields mounts showing striking contrast between the crimson of the stained rubber and the blue-green coloration of the woody tissues and cork cells. After considerable testing of various schedules, he tentatively settled upon the following as giving very satisfactory differential staining to the ground tissues studied, besides being comparatively fast in use.

Soak in potassium hydroxide solution	15 minutes
Add bleaching solution and soak	10 minutes
Rinse with water	
Stain with a mixture of Sudan IV and iodine green (or methyl green) solutions	0.5 hour
Rinse with water	
Mount in glucose sirup	

Solutions used

1. Potassium hydroxide	10 grams
95% ethyl alcohol	100 ml.
2. A commercial bleaching agent (Clorox) containing 5.25% sodium hypochlorite and 94.75% inert ingredients (according to analysis published on the label)	
3. Sudan IV (dye content 86%)	0.095 gram
Acetone	47.5 cc.
70% ethyl alcohol	47.5 cc.
4. Iodine green	0.095 gram
Acetone	47.5 cc.
70% ethyl alcohol	47.5 cc.
5. Methyl green (dye content 60%)	0.095 gram
Acetone	47.5 cc.
70% ethyl alcohol	47.5 cc.
6. A commercial table sirup [Karo (crystal white)] containing, according to the label, "corn sirup, sugar, salt, and vanilla"	

The sample to be stained is placed in a small shell vial to cover the bottom to a depth of about 3 mm. To this is added about 1 cc. of the alkali solution. Sample and solution are thoroughly mixed, care being taken to wet all particles. At the end of the saponification treatment approximately 2 cc. of the bleaching solution are added to the vial, without removing the alkali, and the preparation is thoroughly stirred as before. The sample is then washed out into a cone of tough filter paper and rinsed with three funnelsfuls of water. The sample mass is returned to its vial, dye solutions are added, about 0.5 cc. of each, and the preparation is once more thoroughly stirred. Good differential staining takes place in 30 minutes at room temperature. After the sample is washed out into a Syracuse watch-glass, the water is drained off by capillary

action of a small folded piece of bibulous paper, the dish is refilled, and the water again drained out. The wet sample, transferred to a microscope slide, is collected into a small pile, and the excess moisture is drained away with a bit of bibulous paper. Mounting sirup is added, about 2 to 4 drops, and thoroughly mixed with the sample. With application of a cover glass the preparation is ready for examination.

DISCUSSION

With the above-outlined schedule, rubber is stained crimson, lignified tissues and cork cells bluish green or blue-green. If suberin is not removed prior to staining, the cork cells stain purple or dark crimson, or sometimes partly red and partly green. Although they can with practice be recognized by their distinctive structure, the purple or crimson color is not always clearly distinguishable from the stained rubber, and inclusion of the alkali treatment is accordingly desirable. While Rawlins⁸ specifies boiling alcoholic solution of potassium hydroxide for removal of suberin and Miller¹¹ states that suberin is soluble in warm alkali, the present author has found the alcoholic solution fully effective at room temperature in removing from the cork cell walls of guayule, mariola (*Parthenium incanum* HBK), and coyote brush (*Baccharis pilularis* DC), the material stainable by Sudan III, Sudan IV, Sudan black B, and Calco oil blue NA. Cold aqueous solution does not have this effect nor does 95% ethyl alcohol alone. With other plant species than those with which the author has worked the situation might be different. Each worker must, of course, study his own material.

Although a short treatment with the bleaching solution does not remove pigment completely from the larger tissue fragments, this is of relatively little significance when using Sudan IV as the rubber stain, since in guayule the residual color is a yellow-green which is fully distinguishable from the stained rubber. Entire omission of the bleaching solution results in poorer staining with Sudan IV and iodine green. If both saponification and bleaching treatments are omitted, the Sudan IV-iodine green mixture apparently fails to color rubber occurring in very small amounts, even with a 5-hour treatment. As far as the final staining is concerned, it makes little if any, difference whether the bleaching agent is used before or after the saponifying solution, but the sample is easier to handle when the alcoholic potassium hydroxide solution precedes the bleaching solution.

In this schedule cutin, when present, stains a light pink or lavender color, which is not readily confused with the crimson of the rubber. Leaf veins are dull light green or blue-green.

The question could be raised as to whether the stained agglomerates in unextracted ground samples might not be resin rather than rubber. The texture of these masses, however, is very definitely tough and elastic, indicating that they are at least mainly of rubber. Furthermore, in view of the fact mentioned above that resins and oils are soluble in acetone and in ethyl alcohol, it seems probable that these plant substances are at least in part removed by the solvents used for the alkali and dye solutions.

Another application of this staining schedule is in studying factory bagasse as a check on the completeness of rubber extraction in commercial milling.

The sirup used in this technique, which was suggested by Johansen¹², sets rather slowly, and slides must accordingly be kept for some days or weeks after specimens are mounted. In preparations held for 2 months at room tempera-

ture, the cover glass can be removed only with considerable difficulty, while even those only a month old are fairly well set. Although this sirup mixes freely with water, an excess of water under the cover glass is undesirable because it tends to flow to the edges, subsequently drying out and leaving ragged spaces on the border of the preparation. No mould has developed on any of the author's slides using this mounting medium, the oldest prepared 13 months ago.

It is the author's practice to mix the two dye solutions together at the time of adding to the sample, but they may be combined as much as a week in advance without affecting the final stain. Premixed dyes 4 weeks old gave differential staining, but much less brilliant than the fresher ones. There seems no change in color of the Sudan IV and iodine green staining in preparations even as much as 9 months old.

While the time required for rinsing varies considerably with the material, for many samples mounted slides are ready for microscopic examination within 90 minutes from the beginning of the schedule.

ACKNOWLEDGMENT

The author is indebted to Hamilton P. Traub for the suggestion that Sudan IV and Sudan black B might prove to be rubber-staining dyes.

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